



# Protective and Decorative Coatings

Prepared by a Staff of Specialists  
under the Editorship of

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## VOLUME III

MANUFACTURE AND USES • COLLOIDS,  
OLEORESINOUS VEHICLES AND PAINTS,  
WATER AND EMULSION PAINTS,  
LACQUERS, PRINTING INKS,  
LUMINESCENT PAINTS,  
AND STAINS

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*Dedicated to*

COLONEL GEORGES F. DORiot

ROBERT J. MOORE

WILLIAM HOWLETT GARDNER

AUSTIN O. ALLEN

ALBIN G. SCHUMANN

## PREFACE

This is the third volume of a set of four books dealing with the protective and decorative coatings industry. It covers particularly the subjects of manufacture and uses, specifically of colloids, oleo-resinous vehicles and paints, water and emulsion paints, lacquers, printing inks, luminescent paints, and stains.

Although this series of books, *Protective and Decorative Coatings*, had its inception several years before the Japanese attack on Pearl Harbor, war has had its effect on both the writing and the editing of the last two volumes of the series. In times like these it is a temptation to concentrate on those aspects of paint technology which tend to serve the war effort, especially the armed forces, to the neglect of everything else. But a book like this, which has been years in preparation, and to which the technologists of our industry have unselfishly devoted their time, energy, and knowledge, should be of service during both peace and war periods. It has been directed to those students who look to it for guidance and information, and to the paint industry as a whole, which has kindly welcomed the first two of these four volumes as promising to fill a definite need for a general and comprehensive work that would organize the scattered body of facts and theories on paint technology into a coherent and inclusive whole, on the basis of which new discoveries can be encouraged and classified. It is therefore imperative that no effort be spared to make these volumes useful and authoritative for many years.

And no effort has been spared.

Basic principles have been stressed; they provide a groundwork for the serious student from which he may branch off on new developments of his own. The editor realizes full well that war conditions make obsolete many of the common practices of the industry, and seem to relegate many of its basic principles to obscurity, their places being taken by new basic principles which seem to come into being overnight. But this suddenness of conception is only apparent. It is safe to say that few great discoveries, of principles or anything else, are the result of chance or sheer inspiration. More often they are the result of chance plus a long course of study, training, and work. Each

new discovery builds on the past, and new basic principles are developed from old ones, produced by the same labor which produced the old ones. The main stream of discovery has a perceptible continuity.

To encourage initiative, experiment, and the exercise of native shrewdness and ingenuity, formulations have been kept to a minimum. They are not intended to be the last ones, or the only ones, for the purpose in question, whatever it happens to be. They are given as a guide, as a basis for discussion.

With this general, comprehensive, and organized body of knowledge, the editor is confident that the technical men in our industry will be able to depend on these volumes for reference and guidance for many years.

Turning now to the direct application of this book to the present crisis in our national life, we find the shifting availability of raw materials to be one of the most acute problems of the day. But with a solid technical background the paint chemist can make an effort to meet current demands, and make use of whatever materials are available. Time and again he has worked out a substitute for a necessary ingredient, and then been forced by shortages to devise a substitute for the substitute. Very often the substitute was really an alternate raw material for the same end uses.

Conservation is a second great problem. Certain materials are impossible to get. Certain others can be had, but in greatly reduced quantities, and the prospect of replacement is not certain. It follows, then, that these latter must be used to the best advantage, and, in some cases, not used at all, but reserved for a possible acute need.

The third problem presented by the war is that of meeting specifications. In peacetime, coatings that give good performance may naturally be expected to merit the public's approval. But in war, coatings that give good all-round performance may be rejected because they do not come up to standards in one or two particular tests. In some instances, therefore, test methods and their evaluation have been discussed. It should be realized, however, that the details of test methods and their evaluations may change with the development of further knowledge on the subject, and with the setting of new requirements for the coatings.

Therefore, for particular and detailed information the reader is referred to the various Federal, Army, Navy, Maritime Commission, and other Government Specifications referred to, and to the proceed-

ings of the American Society for Testing Materials. For each specification in question, the latest issue should always be consulted.

As editor of this book, I wish to express my sincere appreciation to the contributors, whose cooperation and sound advice have been invaluable in the preparation of the text.

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JOSEPH J. MATTIELLO

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# COLLOIDS



## CHAPTER 1

# COLLOIDS AND THE PAINT AND VARNISH INDUSTRY

ROBERT J. MOORE

The chemistry of the paint and varnish industry is largely colloidal. Many of the properties of our oils, resins, lacquers, driers, and pigment dispersions are colloidal in nature. Likewise "colloid" is the key word in many other industries. A knowledge of colloidal chemistry is essential to anyone who wishes to understand about bricks, cement, pottery, porcelain, glass, oils, and greases; in soaps and candles, glues and adhesives, it plays an important role; also, in rubber, celluloid, and other plastics, and in leather, paper, textiles, filaments, crayons, inks, roads, and foundry cores. Colloid chemistry is necessary in asphalt, contact processes, and foodstuffs; again, in cooking, washing, dyeing, printing, ore flotation, water purification, and sewage disposal. All branches of pharmacy and physiology deal with colloids because the human body is colloidal. We may sum it all up by stating that colloid chemistry is the chemistry of every-day life (2). Whether we use it or not depends upon our habit of thought.

It has been said that the chief requisite of a chemist is the scientific viewpoint with the habit of visualizing things which go on beneath the surface. When the layman looks at a covered glass cylinder, he sees—an empty cylinder. He may call it a glass jar of air. But the chemist sees more than that. To him there are millions of tiny molecules in constant motion—striking against one another and bombarding the walls of the container and the cover with a pressure approximately fifteen pounds to the square inch.

This kinetic theory of matter gives the chemist his working model or picture of practically all his reactions. If he heats a gas, he notes that the increased energy given the molecules leads to faster motion, greater force of bombardment, greater pressure. If he cools the cylinder, he reduces the energy; the molecules exhibit slower motion and less pressure. He is interested in the quantitative aspects also, and he knows that 22.4 liters of the gas (approximately 1 foot cubed) contains  $6.06 \times 10^{23}$  molecules. The diameter of a gas molecule

would be  $6 \times 10^{-7}$  cm. (0.6 m $\mu$ ). The distance traversed between two collisions is about 10 m $\mu$ ; the velocity is about 1,500 feet per second ( $\frac{1}{4}$  mile per second). (Note: 1  $\mu$  =  $\frac{1}{1,000}$  mm.; 1 m $\mu$  =  $\frac{1}{1,000}$   $\mu$ .)

These dimensions are utterly beyond our physical comprehension. A normal eye at a distance of 10 inches can see objects down to  $\frac{1}{250}$  inch in diameter. With a good microscope objects  $\frac{1}{50,000}$  inch in diameter are visible. But this is about five thousand times the magnitude of a molecule.

Molecular motion is most active in gases, slower in liquids, and still slower in solids. That the molecules are still in motion in the latter two states is readily illustrated by such experiments as the diffusion of heavy liquids up into lighter ones, by the way injured crystals such as salt or alum repair their damage when hung in saturated solutions, without change in weight, and by the diffusion of metal into metal.

### What Are Colloids?

Colloids are merely a state or phase of matter. Any substance may exhibit colloidal qualities if it is dispersed between definite limits of particle size.

There are three classes of dispersion:

1. Molecular (e.g., true solutions of salt, sugar, copper sulfate, etc.).
2. Colloidal.
3. Mechanical (e.g., a suspension of fine sand which may be seen by the eye and which may be filtered out or centrifuged).

### Differences between Molecular and Colloidal Dispersions



<i>Molecular</i>	<i>Colloidal</i>
Clear.	May be turbid.
No Tyndall cone.	Tyndall cone.
No Brownian movement.	Brownian movement.
Diffuse through gels.	No diffusion through gels.
Diffuse through membranes (osmotic pressure).	No diffusion through membranes. (Dialysis—separation of a colloid from soluble salts.)
Freezing point lowered. (Water 18.5° C. for each gram molecule of solute.)	No lowering of freezing point.
Boiling point raised. (Water 5.2° C. per gram molecule of solute.)	No raising of boiling point.

Colloidal dispersions may exist in a gaseous, liquid, or solid dispersion medium. The relative particle sizes of the three dispersion classes are shown in Table I (44).

### Particle Size and the Properties of Colloids

The peculiar properties of colloids are due to their great development of surface. As particles of matter are progressively subdivided, the amount of "surface" increases tremendously. And since amount of surface is the capacity factor of surface energy, the surface energy increases enormously. As an illustration of this increase let us divide a cube having one-centimeter sides by dividing the sides repeatedly into tenths, as shown in Table II.

TABLE I (44)  
RANGE OF PARTICLE SIZE AND PROPERTIES

$\begin{matrix} \text{1 } \mu \text{ [micron]} = \frac{1}{1,000} \text{ mm.} & 1 & \text{[millimicron]} = \frac{1}{1,000,000} \end{matrix}$					
Particle Size		100 mμ	1 μ	10 μ	
	Ultramicroscopic field			Microscopic field (real form may be seen)	
Molecular dispersions	Colloidal dispersions			Mechanical suspensions	
	Pass through filter paper			Retained by filter paper	
	Very rapid			None	
	Brownian movement slow				
	Oil emulsions in water do not separate			Oil emulsions in water separate into two layers	

In colloids the surface is enormous compared to the mass of the substance. Consequently surface forces such as adsorption, capillarity, and surface tension become extremely large and of primary importance. Surface energy does not become noticeable until a specific surface of 10,000 or more is obtained.

Surface areas are readily increased in order to give greater film adhesion. For example, because of minor imperfections average rolled steel sheet has a specific area about twice the measured area. Roughening it with sandpaper increases the surface area about six-

# COLLOIDS AND THE PAINT AND VARNISH INDUSTRY

TABLE II

Length of Sides	No. of Cubes	Total Surface	Specific Surface (surface divided by volume)
1 cm.	1	6 sq. cm.	6
1 mm. ( $10^{-1}$ )	1,000	60 " "	$6 \times 10$
0.1 mm. ( $10^{-2}$ )	1,000,000	600 " "	$6 \times 10^2$ ordinary suspensions and emulsions
0.01 mm. ( $10^{-3}$ )	1 billion	6,000 " "	$6 \times 10^3$ size of cream globules
$1 \mu$ ( $10^{-4}$ )	1 trillion	60,000 " "	$6 \times 10^4$ slight Brownian movement
$0.1 \mu$ ( $10^{-5}$ )	$10^{15}$	60 sq. meters	$6 \times 10^5$ limit of microscope well-defined Tyndall effect
$0.01 \mu$ ( $10^{-6}$ )	$10^{18}$	600 " "	$6 \times 10^6$ typical colloidal solutions hemoglobin molecule
$1 m\mu$ ( $1 \times 10^{-7}$ cm.)	$10^{21}$	6,000 " "	$6 \times 10^7$
$0.1 m\mu$ ( $10^{-8} = 1A$ )	$10^{24}$	60,000 " "	$6 \times 10^8$ atomic dimensions

fold. Activation by alternate oxidation and reduction, which produces a spongy surface, by electro-deposition, or by etching may increase the surface area 1,000 times.

Chemical reactions occur only at surfaces. The speed of reaction in true solution is very great since molecules are reacting. The speed of reaction in the colloid state is much slower. For this we should be thankful since practically all reactions in the human body are colloidal. If these chemical substances comprising our human organism were in true solution, reactions would proceed so fast that we should, so to speak, live 10 years in 10 minutes. Jacques Loeb tried to prove that if he could reduce our body temperatures 10 degrees, we should live over 200 years. The degree of dispersion keeps chemical reaction velocities within certain speed limits through its regulation of free surface and kinetic activity.

## CLASSIFICATION OF COLLOIDS

Various terms have been used in classifying colloids. The term sol is used for ordinary dispersions of particles of colloidal dimensions

in liquids, and the term gel is used for colloids in a solid or semi-solid gelatinous condition. Sols are sometimes called colloidal solutions.

A gel differs from a sol in that a gel is a rigid system that will flow only upon the application of a finite force which is necessary to overcome the forces holding the particles in place.

If the dispersion medium of a sol is water, the sol may be called a hydrosol; if an organic liquid, an organosol; or, more specifically, if alcohol, an alcisol, or if benzol, a benzosol, etc. Similarly a gel may be a hydrogel, an organogel, an alcogel, a benzogel, etc.

Dispersions of solid particles, of colloidal dimensions, in a solid are called solid sols. Dispersions of either solids or liquids in a gas are called aerosols. Dispersions of liquids in either a liquid or a solid are called emulsions.

Colloids are sometimes called lyophobic (Greek *lyein*, to dissolve, and *phobos*, fear) and lyophilic (Greek *lyein*, to dissolve, and *philos*, loving), depending upon the mutual affinity of the dispersed phase and the dispersion medium. If the mutual affinity is small the system is lyophobic; if the mutual affinity is great the system is lyophilic. If the dispersion medium is water the system may be called hydrophobic or hydrophilic as the case may be. If the dispersion medium is an organic liquid the system may be called organophobic or organophilic as the case may be.

We may have lyophobic or lyophilic, hydrophobic or hydrophilic, organophobic or organophilic, etc., sols or gels.

It has already been stated that colloidal dispersions may exist in a gaseous liquid or a solid medium. Dispersions of solids in liquid media are the most important and have been further classified into two distinct groups.

### Suspensoids and Emulsoids

1. Suspensoids (unstable; irreversible—such as iron hydroxide sol, arsenic sulfide sol).
2. Emulsoids (stable; reversible—such as gelatin, albumin, nitro-cellulose).

The contrasting properties of these two classes are: (44)

#### Suspensoids.

1. Very unstable in presence of electrolytes.
2. Show pronounced electrical charge (+ or —) and migrate under electric current according to sign of the charge (electrophoresis).



3. Evaporate to dryness—gel is non-reversible.
4. Surface-tension not much different from that of dispersing medium.
5. Viscosity close to that of dispersing medium.
6. Optically homogeneous to the naked eye.
7. In ultramicroscope show decided optical heterogeneity and energetic Brownian movement.

### Emulsoids.

1. Quite stable in presence of electrolytes (except heavy metal salts).
2. Electrical properties very weak; electrophoresis not marked.
3. On evaporating to dryness generally reversible.
4. Surface tension generally is decidedly lower than that of dispersing medium. (Give persistent foam when shaken with air.)
5. Viscosity decidedly greater than that of dispersing medium and subject to decided increase upon lowering temperature or increase in concentration. (*Examples*—formation of gels; 2 per cent of aluminum stearate in mineral spirits is solid; few per cent of saturated solution of calcium acetate added to ethyl alcohol gives immediate solid gel.)
6. Generally opalescent to naked eye.
7. No striking heterogeneity (light points) when viewed in ultramicroscope. Brownian movement not so apparent. (Colloidal "foot" in linseed oil not easily noted in ultramicroscope.)

### Adsorption

All solids tend to adsorb, or condense on their surface, gases or liquids or certain colloids.

One cubic centimeter piece of charcoal will adsorb on its surface 197 cc. of gaseous ammonia.

One cubic centimeter of charcoal will adsorb on its surface 337 cc. of sulfur dioxide.

*Example—gas masks.* Adsorption of colloids from suspension by charcoal, boneblack, or decolorizing agents. (*Experiment.* Shake copper sulfate and litmus solutions with activated carbon and filter. Copper sulfate true solution—no color change. Litmus, a colloid adsorbed—color removed.)

If the film of condensed air on a small particle remains of the same thickness, irrespective of the diameter of the particle, the ratio of air film to mass of particle will increase as the particle grows

smaller. Thus rock ground to 200 mesh will ~~stave like a liquid~~. The air cushion around each particle makes the ~~grains move over each other like a liquid~~. With a substance like carbon black, which adsorbs gases very markedly, as little as 5 per cent of the apparent volume may be due to the carbon black. A liter of carbon may contain  $2\frac{1}{2}$  liters of air.

Palladium adsorbs nearly 800 volumes of hydrogen. Colloidal platinum adsorbs 3,000 volumes of hydrogen. Patrick's silica gel has a surface of  $2.5 \times 10^8$  sq. cm. per gram and it may therefore be used as an excellent dehydrating agent.

**Adsorption—Liquid by Solid.** If a liquid is adsorbed at a solid surface, it forms a liquid film and we say it "wets" the solid. If the liquid is *not adsorbed*, it does not wet the solid (24, 29).

For a liquid to wet a solid in the presence of air, the liquid must be adsorbed more strongly than the air and must displace it. Some liquids displace air very slowly from solids, in some cases heating being necessary.

If we oil the meshes of a metal sieve, air can pass through but water does not wet the wires and consequently does not go through the screen. Thus gasoline may be freed from water by passing it through a 200-mesh metal sieve. The same principle is used in the shower-proofing of textile fabrics. Fibers are coated with water-repellent hydrocarbons, waxes, metallic soaps of aluminum, calcium, etc., rendering them porous to air but impermeable to moisture up to a certain limit.

Adsorption of liquids by solids is selective. One liquid will be adsorbed more by a solid than another, and consequently one liquid may displace another from a solid.

*Examples:*

Kerosene will displace water from copper.

Water will displace kerosene from quartz.

Alcohol will displace oil from metal.

Linseed oil will displace water from white lead slurry.

Zinc oxide, however, remains in the water phase.

### Moisture on Pigments

There is an adsorbed film of water on practically all pigments. This has been measured on clay powder and found to be a thickness of 50 m $\mu$ . The water adsorbed on quartz is 27 m $\mu$  thick. The necessity of having grinding liquids which are good "wettters" is evident.

In dispersing pigments in either oil, resin, or lacquer vehicles, specific wetting plays an important role with respect to time of mixing and grinding, gloss, and final suspension of the pigment. We call this operation "grinding" but, as we all know, there is practically no grinding in the sense of reducing the grain size. What we do is to break up groups or agglomerates of these grains and rub the surface with the wetting liquid. To realize the important aid that we expect the liquid to give us in the form of adsorption or wetting, compare the relatively large distance between the mill rolls with the much smaller pigment particle diameters (17).

### Surface Tension

Since *specific* surface of finely dispersed systems is enormous, it governs many of the properties we associate with such dispersions. The surface energy of fine dispersions is manifested in surface tension, which is intimately connected with many properties in which we are interested, viz., wetting, flow, flocculation and deflocculation, yield value, and settling. It may be worth while, therefore, to review briefly some considerations regarding surface tension.

Molecules in a liquid attract each other with a force which varies inversely as the eighth power of the distance between their centers. This applies not only to neighboring molecules but also to those many layers away. Molecules near the surface of a liquid are pulled downward by this attraction of the many molecules farther in the liquid, and this inward pull gives rise to the force of surface tension. This inward pull insures that the surface shall always possess the smallest area compatible with other conditions. It gives the so-called surface skin, which can be demonstrated in many ways. It is the reason why a falling drop always assumes a spherical shape since this is the form of least area. It also explains the tendency of two drops to coalesce and become one if they touch.

Surface tension may be measured by means of the Du Nuoy tensiometer, by the relative weight of a falling drop, and by the rise in a capillary tube.

**Changing Surface Tension.** If two liquids will not wet one another or coalesce, we say that there is a high surface tension or interfacial tension between them. Thus mineral spirits and water shaken together immediately separate into two layers. This high surface tension may be shown by counting the large drops from a medicine dropper of water slowly emptied under the surface of the mineral spirits (1 dropper averaged 70 drops).

If now we add a colloid to the water, the finely dispersed material is drawn to the area of greatest attractive force. That is, it tends to be pulled to, and concentrate in, the surface layer. (If we analyze the soap foam from water, we find a higher concentration of soap in the foam than in the remainder of the dispersion.) Since, then, part of the forces of attraction are shared by the colloidal particles, the pull on the surface molecules becomes less, and we say that surface tension has decreased. Thus, if we add a colloid (few drops soap dispersion) to the water-mineral spirits mixture, we get a fair degree of emulsification on shaking. The drops of water from the medicine dropper are much smaller and now average about 400 per dropper. The lowered surface tension of the interface is insufficient to hold a large drop. All colloids tend to reduce the surface tension between liquids and liquids, and liquids and solids.

### Specific Wetting

There is another factor involved in coalescence of two materials which we may call the "specific-wetting value" of one for the other. The molecules must have a definite adhesive force which enables one to wet the other. This difference may be illustrated with the medicine-dropper test as used above.

1 dropper refined linseed oil into water = 44 drops

1 dropper linseed fatty acids into water = 300 drops

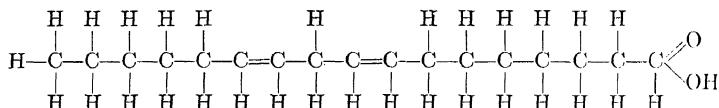
The fatty acids have a much greater specific-wetting value for water. Another way of differentiating specific wetting is to see how far a drop flows out on a "clean" solid or liquid surface. Oleic acid on water flows out to a film one molecule thick. Comparative tests may be made by the Langmuir method of measuring the height of a drop on a solid, or measuring the contact angle (4). A small angle (film flowed out) is good wetting; a large angle (high drop) is poor wetting (3).

### Wetting and Polarity

The explanation of wetting is still not entirely clear and is undergoing marked transition. But molecular polarity is playing an important part in its development. Polar liquids are those in which the molecules are unsymmetrical and contain both active or polar and inactive or non-polar groups. The polar groups vary in degree of activity, and so polar liquids vary in degree of polarity. A result of the polarity of liquids is the orientation and packing of molecules

in a surface layer. That is, in any liquid (e.g., an organic hydrocarbon) the molecules arrange themselves in such a way that their chemically active portions are attracted inwards, leaving the least active portion of the molecules to form the extreme surface layer. According to Langmuir (22) this surface orientation or turning of the molecules is the principal factor in the surface energy of liquids. The active end of the molecular chain is called the polar group whereas the more stable, inactive end is the non-polar. The presence or absence of polar groups largely determines whether or not a liquid will spread over a surface. The spreading of an oil upon water (demonstrating good wetting) is often due to the presence of an active group in the molecule, that is, some group which has a marked affinity for water. Thus linoleic acid spreads on water to a film 1 molecule thick due to the presence of the carboxyl group ( $\text{COOH}$ ) which is oriented to the water surface. Oils (such as mineral spirits of paraffin base) without such active groups do not spread or wet to this degree.

For the linoleic acid ( $\text{C}_{17}\text{H}_{31}\text{COOH}$ ) having the long chain formula as follows:



the great affinity of the water for the very polar  $\text{COOH}$  group tends to turn this group toward the water interface and thus gives a low surface tension.

In the liquid hydrocarbon of the paraffin series, the molecules arrange themselves so that the methyl groups ( $\text{CH}_3$ ) at the non-polar end of the chain form the surface layer. This surface layer therefore is the same no matter how long the hydrocarbon chain may be, from light gasoline ( $\text{C}_7\text{H}_{16}$ ) to the heavy  $\text{C}_{20}\text{H}_{42}$ . The compounds from hexane to molten paraffin all have the same surface energy although their molecular weights differ widely.

Alcohols, such as  $\text{CH}_3\text{OH}$  and  $\text{C}_2\text{H}_5\text{OH}$ , likewise all have the same surface energy since their  $\text{CH}_3$  groups are all oriented in the surface with their polar groups drawn in towards the center.

Now, considering again the experiment above with mineral spirits and water, there is initial high surface tension since there is no polar group in the hydrocarbon. When we introduce a small amount of organic material (sodium oleate), which is partly polar to water and

partly to the hydrocarbon, we decrease greatly the free surface energy. We then have a tendency to emulsify on shaking and we say that wetting has increased. Whenever we reduce the surface tension between two liquids or between a solid and liquid, we have changed the orientation of the active groups to the surface layer where they may wet another substance.

### Peptization

Certain solutions will peptize or disintegrate certain precipitates to give us colloidal dispersions. This is always the result of adsorption. We may achieve this colloidizing effect by means of (a) a liquid, (b) an adsorbed ion, or (c) a protective colloid.

#### *Examples:*

a. *Liquid.* Butyl acetate peptizes nitrocellulose. Neither alcohol alone nor ether alone will, but their mixture will peptize nitrocellulose.

b. *Adsorbed Ion.* Occasionally in precipitating a charged colloid by an ion of opposite charge, an excess of the ion will redisperse the colloid having the same charge as the ion.

c. *Protective Colloid.* If we attempt to precipitate silver chloride in the presence of an emulsoid colloid such as gelatin we have a stable milky dispersion.

Peptization is in reality deflocculation, a dispersion of groups or agglomerates into separate particles which once more obtain active motion and remain suspended. The detergent effect of soap is to deflocculate particles of dirt, etc., mechanically held or adsorbed on a textile or skin. These water-peptizable colloids like gelatin, gum arabic, dextrine, soaps, or saponin will peptize many precipitates and are therefore called protective colloids. They prevent the agglomeration and consequent settling of finely divided precipitates (32).

**Peptizing and Pigments.** Peptizing effect is frequently used in the suspension of pigments. A minute amount of tannic acid, turkey red oil, metallic soaps, or similar colloids will cause a pigment to deflocculate readily on grinding with oil.

Aniline dyes, which are insoluble in solvent naphtha, may be peptized by zinc or magnesium resinate. Gum arabic is often added to water stains to render the dye more stable.

A protective colloid frequently prevents the formation of a precipitate when it may not be able to disperse the same precipitate after it is formed. New dyes and certain of our pigments are frequently coated with protective colloids for easier wetting and better suspension.

An example of deflocculation is shown by Prussian blue. Shaken with mineral spirits, it may be filtered out. But shaken with raw linseed oil (containing protective colloids), it is peptized and passes through the filter paper.

Colloids may be adsorbed and suspended by certain surfaces or they may be adsorbed and removed by others. For example, the tremendous surface of fuller's earth or activated carbon is able to adsorb the colloidal coloring matter in oils and is therefore used for bleaching. The colloiddally held driers, such as lead and cobalt, are frequently removed from our paint vehicles by the colloidal alumina of organic lake pigments or by surface adsorption on carbon black.

### Pigment Grinding and Dispersion

It is evident that colloidal properties affect many of our problems in the grinding, floating, and leveling of pigmented products. The Cleveland Production Club in its series of five papers on the subject of pigment dispersion found this to be true (33). In this investigation many colloidal factors influenced the results. Among them were particle size, occluded gases, electrostatic charge, dispersing and wetting agents (rosin acids, stearate, and methyl cellulose). They found further that relative specific gravity is not an important factor in pigment floating.

The St. Louis Production Club found (34) in tests on pigment dispersion that "acid value, surface tension [measured by the Du Nuoy tensiometer], and relative interfacial tension against water [Gardner [16]] are *not* indicative of the grinding efficiency of a vehicle." Colloidal wetting agents did give interesting results.

The Technical Committee, New York Paint and Varnish Production Club, has also published interesting papers on the effect of wetting agents on dispersion. The first of these papers, entitled "A Study of Pigment Wetting and Dispersion" (36), investigated the effect of fourteen different agents on the dispersion of fifteen white and colored pigments. The agents used were zinc naphthenate, oleic acid, ethylene glycol, triethanolamine, diethylene glycol monoethyl ether (carbitol), butyl stearate, benzaldehyde, nitrobenzene, ester gum, Twitchell Base 265 (a sulfenated compound), emulsiphor A, lecithin, salicylic acid, and XJ-7488, a proprietary wetting agent. Experimental work divided the pigments into hydrophilic and hydrophobic types. Results showed that a number of the agents were effective with hydrophilic pigments, but in no case were the hydrophobic pigments aided. The conclusions were that the same agent was not the

best for all pigments. The agents in the list which showed highest general utility were lecithin, zinc naphthenate, and XJ-7488. However, others were more effective with certain pigments, as shown in their Table 26.

A second New York Club Technical Committee paper was entitled "Properties of Linseed Oil, Heat Bodied in Air and Vacuum, and Its Behavior with Pigments, with and without Wetting Agents." One of the conclusions in this work was that added wetting agents tended to minimize the differences between air-bodied and vacuum-bodied oils in regard to pigment dispersion (37).

J. A. Riesling (30) investigated the electrostatic responses of dispersed pigments in relation to flooding, dispersion, and flocculation. In paint formulation the particular charge on the pigment particles appeared to have fundamental significance in relation to the above properties. His data show that in a dispersion of mixed pigments in paint, the particles carry either a positive or a negative charge, with flooding present if a wide range exists in the particle size. This was found true also by the Cleveland Club when Prussian blue was carried into colloidal dispersion from chrome green, leading to a blue float. Continued grinding to reduce also the average particle size of the remaining chrome yellow gave a satisfactory green color without the float.

The pretreatment of pigments to give easier dispersing action is also growing in interest. Cataphoresis experiments with titanium oxide show (21) that the maximum deflocculation of pigments is obtained when the particles are coated with a unimolar layer of deflocculating agent. Protective colloids to give better dispersion are widely used in other industries. For example, such colloids are added to ice cream to give a smooth velvety texture. Unless the ice cream contains such protective colloids (eggs, gelatin, etc.), it becomes gritty or grainy on the palate. Less than  $\frac{1}{2}$  per cent gelatin is necessary. Its presence tends to inhibit the crystallization of water and stabilizes the casein, making it easier to digest. This stabilization of cream and milk prevents coagulation and is frequently used in infant feeding. The fats and casein are kept dispersed and flocculation is avoided.

Another method of pretreatment for easier dispersion has recently been described by Bartell and Murray (5). They find that pigments, such as carbon black, may be made strongly organophilic (readily wetted by organic liquids) or by appropriate treatment can be made hydrophilic so that it is more readily wetted by water. Mild oxidation with ozone was employed.



### Flocculation and Yield Value

The paint man prefers to speak of the "body" or consistency of a paint since viscosity is not a true measure of fluidity of such a heterogeneous colloidal system (6). Such characteristics of plasticity bring into consideration the measurement of yield value and the thixotropic state. Morrell and Wornum (26) describe the capillary tube plastometer of Bingham and Green to show that paint follows the law of plastic and not viscous flow, and that its consistency is dependent upon yield value and mobility. The yield value is the pressure required before paint movement through a capillary tube can take place and in practice manifests itself as "shortness."

Polar colloids (e.g., aluminum stearate) have very slight influence on the mobility of paint but have extraordinary effect in raising the yield value (9). Moisture exerts a great effect on the plasticity of paint,  $\frac{1}{2}$  per cent in a certain paint raising the yield value from 90 to 3,450 and at the same time reducing the mobility to one-fourth of its original value. Deflocculation and reflocculation are suggested as being due to orientation of molecules of the viscous phase at the boundary surfaces of the unshearable phase.

The flow and leveling properties of high-grade enamels are easily affected by relatively small additions of substances which change the wetting and degree of flocculation. For example, several plant batches of a zinc oxide-long oil enamel showed bad brush marks due to poor leveling out. In all other physical tests these batches were up to standard. Many changes were made in the thinners, driers, oils, etc., but the poor leveling persisted. Then the effect of small amounts of various additive agents was tried. It was found that one-tenth of 1 per cent salicylic acid (on the weight of vehicle) stirred in as a solution in warm turpentine restored perfect leveling. Whether this result was due to wetting effect of the acid or of the zinc salt produced has not been decided. The Du Nuoy tensiometer values appear to have some relation to leveling properties, as shown in Table III.

It will be noted from the results in Table III that the Du Nuoy tensiometer values increased from 32.4 to 50 in fairly close agreement with the relative leveling values arbitrarily given as one (1) for the best and nine (9) for the poorest. The viscosity cup and flow meter values showed no relation to the leveling characteristics.

S. Cabot (35) shows that such pigments as zinc oxide, titanium-barium, and lampblack may be dispersed to colloidal fineness in the

TABLE III  
ENAMELS AND PAINTS IN ORDER OF LEVELING PROPERTIES

	Relative Leveling (By Brushed-Out Panels)	Du Nuoy Tensiometer	Viscosity (Ford Cup)	Flow-Meter * Values	
				15 Sec.	90 Sec.
1. White Enamel #7 + ½% Salicylic	1 (Best)	32.4	360	7.0	9.0
2. Q. D. White Enamel	2	32.1	84	9.0	11.5
3. White Enamel	3-4	34.5	517	7.0	9.0
5. White Enamel	4-3	33.0	630	7.0	8.5
6. Mill White	5	33.0	308	8.0	10.0
7. #1 Original without Salicylic	6	36.6	380	7.5	9.2
8. Enamel Undercoat	7	39.0	Too short	4.5	6.2
9. White Lead House Paint	8	44.5	70	8.0	8.5
10. Mixed House Paint	9 (Poorest)	50.0	108	6.2	6.5

\* Gardner, "Flow-meter," *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors*, 9th Ed., p. 232, 1939.

usual paint thinners, especially in the presence of a protective colloid such as heat-treated drying-oil gels. Irreversible gels such as polymerized tung oil may be peptized by simple mastication with the proper amount of pigment.

### Emulsions

Two types of emulsions are met with in drying-oil systems: first, the oil-in-water type, illustrated by emulsified resin paints; second, the water-in-oil type, illustrated by many oleoresinous paints containing a substantial amount of water. This type is also illustrated by certain varnish or oil films turning milky or opaque on immersion in water. The emulsifier for the water paint is a partially water-soluble colloid which is adsorbed at the boundary oil-water surface and lowers the surface energy between the liquids (8). An excess of adsorbed positive ions in the paint leads to water-in-oil emulsions; an excess of negative ions produces the oil-in-water type. The same principle applies to polishing wax emulsions. The introduction of new synthetic emulsifying agents which are not affected by electrolytes will probably do much to increase interest in this growing field.

The mechanism of adhesion of paint films to metals has been studied recently by Dr. P. H. R. Nettman (27). He examined the micro-crystal structure of the paint-metal interface, using as unit of measurement the wavelength of X-rays. He points out that the formation of submicro points of adhesion between metal and air, and the oils, pigments, driers, etc., in the coating is governed by distinctive principles. Minimum energy consumption is concomitant with the merging of the fine-structure lattice of the same or very similar patterns. Thus metals prefer metals, fats choose fats, oils and resins choose their like, while, according to Nettman, "the catalysts or liaison officers are the metal driers." Whether this latter point is due to the orientation of the polar ends of surface molecules because of the drier catalysts would make an interesting investigation.

### Ultrasonic Dispersions

Ultrasonics have recently been studied in connection both with the dispersion of liquids and solids, and also in their coagulation. Under the stretch of the high-frequency sound waves the liquid disrupts and the phenomenon is always accompanied by a hissing sound.

Ultrasonics may cause all sorts of dispersions from emulsions to fogs, and they may also bring about coagulation. Sollner (38) used the technique described by Wood and Loomis (42). Plates about 7 cm. in diameter and 1 cm. thick, cut from quartz crystal, are placed on a lead electrode and covered with a brass-ring electrode. The whole system is immersed in transformer oil, an alternating field is applied, and the quartz, which is strongly piezoelectric, starts vibrating. Since the electrical frequency is the same as the mechanical frequency of the quartz plate, the vibrations are so pronounced that the oil over the quartz is set in motion and a fountain of oil rises over it. Although the quartz disks used had frequencies of about 200,000 cycles a second, the frequency employed is immaterial. To produce emulsions a test tube containing the immiscible materials is dipped in the oil fountain and emulsification begins at once. For example, mercury and water immediately give gray clouds of finely dispersed mercury thrown into the water from the mercury-water interface. Or immiscible liquids, such as benzene and water, will give under these experimental conditions about 60 grams of dispersed benzene in one minute. In the presence of suitable emulsifiers very high concentrations can be obtained.

The peptizing effect of ultrasonic waves on gel-like substances, precipitates, and gels has frequently been investigated (39). All such

systems, which are characterized by containing preformed particles of colloidal or semi-colloidal size, may be easily separated from each other.

B. Claus (11) disperses ultrasonically metals being deposited by electrolysis. Here the metal is not deposited as a coherent mass at the cathode but redispersed at once as a semi-colloidal liquid.

The best examples of substances comparatively easily dispersed ultrasonically in water to yield colloidal solutions are crystals of mica, gypsum, haematite, sulfur, graphite, etc. It is advisable to use instead of pure water, a solution of a suitably chosen electrolyte (ammonium hydroxide) in order to charge the particles, preventing their coagulation.

Freundlich and Gillings (15) describe the influence of ultrasonic waves on the viscosity of colloidal dispersions. We can liquefy thixotropic dispersions by mechanical shaking or stirring and we can duplicate this effect by the high-frequency shaking (vibration) of ultrasonic waves. Such experiments have been made with dispersions of gelatin, gum arabic (20), sodium stearate, and methylcellulose (19). The effect is ascribed mostly to a degradation of micelles, or macromolecules. The high *normal* viscosity of solutions of glycerol or concentrated sodium lactate is not affected by ultrasonics.

Recently a rigid all-metal oscillator has been placed on the market designed for the production of "sonic" (soft-curd) milk. One pass through this machine at the rate of 250 gallons per hour on a frequency of 360 cycles per second is sufficient to give a complete dispersion of all butter fats and render the milk more digestible (Submarine Signal Company, Boston, Massachusetts).

It is possible to disperse tough, difficultly soluble, highly polymerized resins rapidly by sonic oscillation. This modern procedure offers interesting possibilities for new development in the paint and varnish industry.

In this chapter we have presented the subject of the kinetic theory and the colloidal state of matter and have pointed out many of the ways in which this subject touches the paint and varnish industry. The section on dispersion alone is of fundamental interest in the industry. The story, of course, is only partly told. But it is a fascinating subject and one which during the next few years of active research will do much to improve our knowledge of paint fundamentals.

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## CHAPTER 2

### POLYMERIZATION METHODS

ALFRED E. RHEINECK

Perhaps one of the most time-consuming operations in the manufacture of paints and varnishes has been the preparation of bodied oils. Compared with other operations this is a costly factor, and within the last fifteen years many attempts have, therefore, been made to find ways and means to overcome this handicap.

With the introduction of tung oil, oiticica oil, and, more recently, dehydrated castor oil, a heat treatment of these oils has been for a different purpose, namely, to "gasproof" and to prevent wrinkling and frosting of film of the finished product. Rarely in varnish making are these oils heated alone; usually resins are added. The degree of heat and time necessary to gasproof are usually a function of the resin. With dehydrated castor oil it is possible to prebody considerably before the resins are added. With oils of the linseed type, gasproofing is not the problem. Many processes have been devised whereby tung oil can be bodied without the addition of resins.

The literature is abundant with information and theories regarding the changes that take place during these bodying processes. In the end, there probably is not a great deal of measurable chemical difference in the polymers produced by the various processes, although some physical differences are noted by the effect produced in finished products. It is not the purpose of this chapter to consider the changes that take place in heat bodying or the differences in the variously bodied oils since these have been considered in Chapter 3. It is, however, the purpose of this chapter to review the various methods used by the protective-coatings and petroleum industries to produce bodied oils.

The methods used to produce thickened or polymerized oils can in general be classified as follows:

- I. Polymerization by physical means.
  - a. Heat.
  - b. Pressure.



- c. Radiation.
- d. Electrical discharge.
- II. Polymerization by chemical means.
  - a. Addition of various reagents.
  - b. Oxidation—blowing.
- III. Polymerization by combination of any of the above.
- IV. Segregation of polymers of high molecular weight.
  - a. Selective precipitation (solvent extraction).
  - b. Distillation.

The application of these methods has been prompted by attempts industry is making to reduce the time and labor required for the preparation of stand oils.\* This is not necessarily the only reason because the attention has also been focused in the direction of removing the products of decomposition which are invariably formed during the heat polymerization of oils as well as to improve the quality of the bodied oils. Unless special precautions are taken, these products for the most part remain in the thickened oils. The removal of these products has been the basis of considerable work toward improving the design of heat-processing equipment. The orthodox method of the varnish maker (bodied oils in open kettles) is being gradually superseded by more modern methods, in which closed kettles and vacuum are used.

The difference in constitution of tung oil and oils of the linseed, soybean, perilla, and fish types determines the rate of thickening and the equipment needed. The processes employed in both cases are somewhat different. Tung oil lends itself very readily to a continuous process; since this oil gels very readily processes have been so arranged that the methods used tend to minimize this danger. The chemical treatment of oils is applicable to both types, but has been concentrated largely on the linseed type.

For the most part polymerization usually applies to oils. There are, however, several instances in the discussion which follows where the fatty acids of the respective oils are polymerized and then esterified. Such processes are not general because of the extra steps involved before the finished product is obtained.

#### PHYSICAL PROCESSES

Oil processing by heating is well known in the art. Open kettles over open fires are still common, and as such need no further discus-

\* Refer to pages 47-48, Chapter 3.

sion. Under this caption such processes which are unique and "novel" are considered, although heat is used in the majority of cases.

A *continuous process* for treating or "thermolyzing" tung oil has been devised by Reece (43), in which case the oil is rapidly forced through a conduit of restricted cross section at about twenty-five pounds pressure at 625° F. (329.5° C.) and then rapidly cooled to avoid gel formation. The oil produced by this treatment is claimed to have vastly superior drying qualities, i.e., it dries to a smooth film.

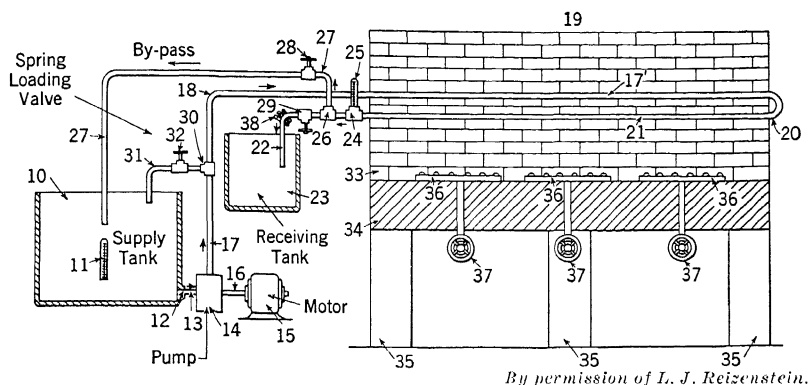


Fig. 1. Polymerization Methods.

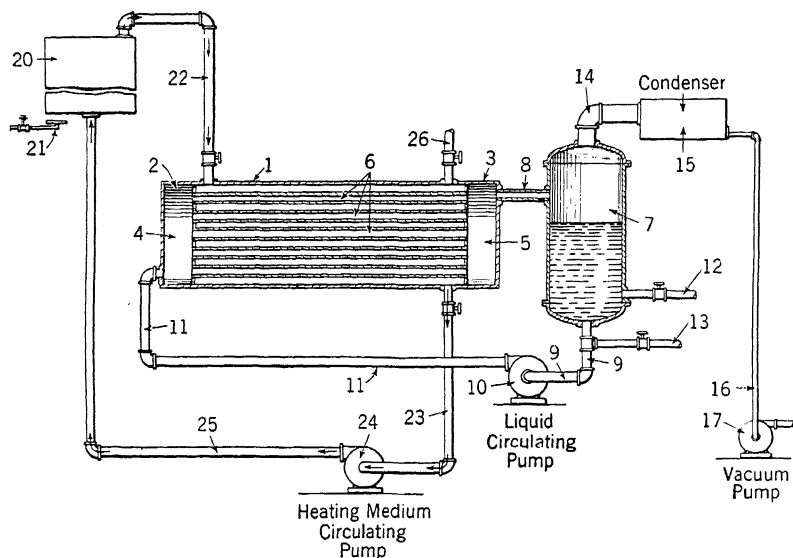
The oil in the reservoir, 11, is passed through a pump, 14, through a conduit, 17, 17', and 21, through the heating zone, 19. The effluent from the heating zone can be passed into the receiving tank, 23, or by-passed through a pipe, 27, and a valve, 28, to the reservoir, 10.

A non-drying, plasticizer type of oil is produced when higher temperatures, i.e., 700–900° F. (371.1–482.2° C.) are used. This process has also been modified by Reece and Taggart (44) so that mixtures of soybean and tung oil are similarly treated; it is also claimed that it applies favorably to linseed oil. Somewhat similar continuous processes for heat-bodilyng tung oil have been described by Wolf (64) and Reizenstein (45). The type of apparatus is shown in Fig. 1.

Modifications in this process and equipment to effect the removal of volatile constituents and to obtain a more uniformly polymerized product, using lower pressures, were introduced by Ward (60). Badger (7) has described improvements in heating an apparatus for this purpose, in which the usual high-temperature zones are heated with diphenyl and diphenyl oxide vapors (Fig. 2).

For some purposes oils are polymerized in closed systems and under pressure. Harris and Sutherland (23) polymerized oil by heating in

a closed automatically controlled kettle just below the carbonizing point, at which time the heat is shut off. The polymerization is continued by the heat given off in the exothermic reaction at this point. Later, improvements in kettle design were introduced to remove volatile products. Schneider, Flugge, and Evans (48) produce



*By permission of W. L. Badger.*

FIG. 2. Polymerization Methods.

The heating chamber, 1, consists of small diameter tubes, 6, connected into two headers, 4 and 5. The oil is circulated through the tubes into reservoir, 7, under partial vacuum which permits decomposition material to escape. The heating medium is vaporized and heated in boiler, 20, and conducted into chamber, 1, where it is partially condensed and returned to the boiler via a pump, 24.

quick-drying oils by saturating them with carbon dioxide at atmospheric pressure and then forcing the oil through an orifice at 1,000 pounds per square inch pressure at 500–700° F. (260.0–371.1° C.), whereupon light-colored oils result. Starkweather (56) mentions that he polymerized wood oil at 500 to 6,000 atmospheres pressure at 122° F. (50° C.) and found it to be not unlike the polymer obtained in the usual way. Fawcett, Gibson, and Perrin (16) claim improved drying properties for linseed oil bodied under pressure. A comparison of the properties of oils bodied at atmospheric and 300 atmospheres pressure by this process at 617.0° F. (325° C.) for 1½ hours is made

in Table I. These investigators have also applied their pressure process with equal success to fatty acids.

The solidification of tung oil on heating has been a source of trouble in many cases. Accordingly, several processes are mentioned in which attempts have been made to overcome this difficulty and still have an oil which would not frost on drying. In common practice tung oil gelation can be prevented by rapidly mixing the hot oil with a prepolymerized hot oil, i.e., linseed oil. Geiger and Burgess (21) recognized the difference in the type of tung oil polymers formed at

TABLE I  
CONSTANTS OF BODIED LINSEED OIL

	Oil-Bodied at	
	Atmospheric Pressure	3,000 Atmospheres
Viscosity	7 poises	103 poises
Iodine value	127.6	123
Acid value	13.5	9.4

high and low temperatures. In order to effect the formation of the high-temperature polymer without gelation, the oil was bodied at 600° F. (315.5° C.) in 40 per cent solvent such as high-flash coal tar naphtha, under pressure for a given period in a specially designed apparatus. After the completion of the heating process the solvent is removed either by steam or vacuum distillation. As a means of preserving the bodied oil, Alvarado (1) finds that improved properties can be had by aging bodied tung oil in a solvent, e.g., mineral spirits, in contact with air.

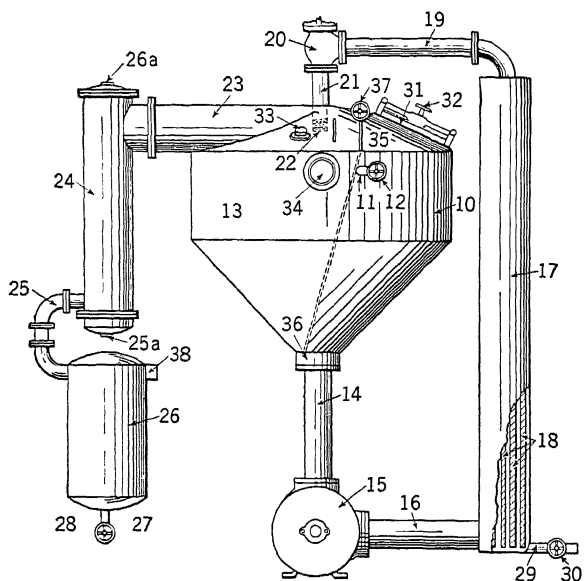
The properties of oils prepared by some of the above processes are shown in Table II.

A number of processes using an ordinary vacuum are described in the literature. Their aim is to reduce the amount of decomposition products in an oil and to improve the final color. In batch processes, a vacuum of 26 inches or better at temperatures of 580 to 620° F. (304.4–327.7° C.) will remove fatty acids, acrolein, water, and the usual decomposition products. Oils treated in this manner have acid values ranging between 5 and 10. When lower acidity is required, various

TABLE II  
CONSTANTS OF TUNG OIL BODIED BY VARIOUS PROCESSES

	Geiger and Burgess (21)	Reece (43)	Schneider, Flugge, Evans (48)	Original (30)
Specific gravity	0.967	0.915		0.936
Saponification value	188.8	183	195.6	193
Iodine number	142.6	113	114	150
Refractive index	1.50450	1.5020		1.5180
Acid value	3.5	5.1	9.3	

modifications in equipment are introduced such as that described by Harrison and Batchelder (24), Fig. 3, in which the oil is sprayed into a vacuum chamber, of a pressure of a few millimeters of mercury



*By permission of the California Ink Co.*

FIG. 3. Polymerization Methods.

The oil to be polymerized is placed in the vacuum pan, 10, and circulated by a pump, 15, up through the tubular heater, 18. When the oil reaches the nozzle, 22, it is atomized, the oil falling into the vacuum pan, while the vapors leave via a tube, 23, into the condenser, 24.

so that the volatile and acidic portions escape, while the polymerized material remains.

The bodied oil can have an acid value as low as 2.0. According to Kaempfe (31) train oils can be heated and blown with superheated steam, which causes the acidic portions to distill. In this connection, the removal of the distillate can be aided by applying a partial vacuum to the system. A similar Dutch process (29) indicates that the oleic and saturated acids distill over first, followed by the polymerized acids which are then esterified with glycerol. Rossmann (47) claims that oils of an initial inferior quality can be converted into satisfactory stand oils by processing in a vacuum of 10 mm. of mercury or less between 572.0–752° F. (300–400° C.). Korzulin and Konoplev (32) state that high-vacuum processing reduces the tendency to flash and accelerates bodying due to removal of free fatty acids. Zinov'ev and Orlov (65) describe a continuous vacuum-bodying process in which they use temperatures higher than usual, viz., 671° F. (355° C.). For linseed oil, this high temperature is necessary. Apparently, difficulty was encountered when this was translated to production. A method of thickening oils of the linseed type and combining with resins is described by Briscoe (10). In his process oils are circulated between kettles and heaters, the latter being constructed so that the volatile decomposition products are removed by the vacuum maintained in the system.

That the vacuum plays an important part in the bodying rate of an oil is shown in Table III, by Wasson and Frölich (61). These investigators were primarily interested in polymers of the oils of the semi-drying type for petroleum admixtures.

In the process of Hill and Walker (27), the fatty acids are pre-polymerized. The acids are preheated for 17–18 hours at 509.0–527.0° F. (265–275° C.) under passage of carbon dioxide. This is followed by a vacuum distillation at a pressure 2–3 mm. of mercury so that the unpolymerized portions are removed first, leaving the still residue to be esterified with glycerol.

The bombardment of an oil film by *cathode rays* was shown by Long (36) to cause semi-drying and drying oils to set to solid films. This process is one of polymerization rather than the conventional drying of an oil film.

The use of an *electrical discharge* to produce solid gels "Votol-faktis" is the basis of several patents. Hock and Nottebohm (28) showed that the viscosity of linseed oil could be increased by a silent discharge; molecular aggregates were formed which precipitated

TABLE III  
COMPARATIVE BODYING RATES OF RAPESEED OIL (61)

Time, hours	Viscosity Sayboldt at 210° F. (98.9° C.) for Oils Bodied at	
	Atmos. Press.	5 mm. Hg
0	60	60
4	...	200
8	...	700
10	...	1,750
12	140	
20	155	
27	165	

as an insoluble solid. According to Slansky and Götz (52), vegetable oils subjected to a *luminous electrical discharge* of 7,000 volts and a frequency of 600 cycles were converted to a valuable stand oil. A bodied oil suitable for use in lubricating oils can be prepared by the method of Richardson (46), i.e., subjecting a partially hydrogenated fish oil in a trommel type voltolizer at a pressure of 466 mm. of mercury and a potential of 4,000 volts at a frequency of 10,000 cycles per second.

Improvements in the ester type lubricants made by polymerizing oils by an electric discharge are claimed by Gaylor and Turner (20a). In this process the polymerized oil is "stabilized" by hydrogenation after the thickening process.

### CHEMICAL PROCESSES

The polymerization of oils can be accelerated or promoted by the presence of many agents, e.g., metals, salts, halanhydrides, and numerous organic compounds.\* In most cases, these agents are perhaps "catalysts" which merely promote polymerization rather than react chemically with oils. Chemical reagents act on oils of both types. Usually the oils of the tung variety respond more readily to these

\* For a complete list of these compounds in addition to those mentioned in this section the reader is referred to the original patents (2, 3, 4, 5, 6, 42, 49, 53) and reference 38.

compounds than do oils of the linseed type. There are some instances where a definite chemical combination takes place between the oil and reagent.

*Metallic* catalysts such as nickel, platinum, palladium, cobalt, copper, and iron, and *chlorides* such as aluminum chloride, stannic chloride, and antimonous chloride, and various *oxides* and "*per*" compounds located in a "polymerizing zone," through which the oil passes continuously, are claimed by Priester (42) to accelerate the bodying of linseed oil. *Finely divided metals*, platinum, palladium, copper, iron, nickel, or cobalt, deposited on asbestos or kieselguhr accelerate bodying at temperatures between 392.0–608.0° F. (200–320° C.), preferably in the presence of an inert gas as carbon dioxide or a vacuum (39). According to Krumbhaar (35), cobalt, manganese, and iron are colloidally dispersed under high potential in alcohols, e.g., butanol; the solution is then added to the oils to be polymerized. Upon heating to 530° F. (276.7° C.) the colloidal metal disappears and the oil bleaches and thickens.

Gases, e.g., sulfur dioxide and hydrochloric acid, are about equally effective in promoting polymerization of stand oils. Van Vlodrop and Waterman (59) prefer the dry sulfur dioxide, and claim that stand oils treated in this manner are superior to those treated in the usual manner. Van Vlodrop (58) says that oils with an initially inferior color become bleached by this process.

The petroleum industry has become interested within recent years in boron fluoride catalytically bodied oils as addition products to lubricating oils and greases. Eichwald (15) and Whiteley and Turner (62a) use this reagent to polymerize drying and semi-drying oils below 392.0° F. (200° C.) with or without solvent. Eichwald's process also provides a method for washing the treated oils to remove excess reagent. Whiteley and Turner disclose a method of copolymerizing oils with petroleum derivatives. In another process (55) polymerization is effected by bubbling boron fluoride through a hydrocarbon solution of the oil.

The heating of other boron compounds, e.g., borax, boric anhydride, and boric acid, with oils bearing hydroxyl groups has been described by Colbeth (13). The oils so treated are useful in lacquers and form products which can be molded either with or without pigments.

Brendel (9) states that tung oil can be bodied at either high or low temperatures. The latter condition is safe but the tendency to crystallize on drying is not overcome, whereas at the higher temperatures the oil is not stable and tends toward gelation, yielding a non-



crystallizing oil. However, the addition of sulfur or sulfur-containing compounds changes the nature of the oil to a marked degree, making it possible to body it without difficulty at any temperature. Gardner (20) proposes the heating of the oil with sulfur or sulfur-bearing compounds, the sulfur being removed by the introduction of copper gauze. Donovan and Daniels (14) blow the sulfur-treated oil with air to cause another reaction. Harper (22) treats tung oil similarly with small percentages of selenium, but removes this reagent by extracting and washing the cold oil with alcohol. Both the Gardner and Harper treated oils are claimed to dry to smooth films, whereas Donovan and Daniels state definitely that the oil does not dry, serving merely as a lacquer plasticizer. In each case, these oils acquire considerable body. The effect of sulfur and sulfur-bearing compounds is important. According to Foulon (18) oils treated with sulfur chloride are becoming available. The treatment of semi-drying and non-drying oils with sulfur chloride converts them into oils which possess film-forming properties and as such are added to varnishes. In this case a definite compound forms between the oil and sulfur chloride.

Sodium bisulfite in small quantities is claimed by Sekken (51) to accelerate the polymerization of fish oil when heated in a closed vessel at about 527° F. (275° C.).

Carbonyls, e.g., nickel, iron, cobalt, manganese, and the like, are used by Ambros and co-workers (2) as 1 or 2 per cent of the weight of the oil and when heated at 572° F. (300° C.) in the usual manner accelerate the thickening of oil. A normally thick oil is obtained in four to five hours whereas gelation is complete in five or six hours.

Although it is known that aluminum naphthenate is a thickening agent, Stadnikov *et al.* (54) claim that oils heated with this reagent in the presence of air body in a shorter time than those not so treated.

According to Wilborn and Rieger (63) at 464° F. (240° C.) thallium compounds as the resinate or naphthenate accelerate the bodying rate.

A great number of *organic reagents* have been claimed to accelerate polymerization of oils. Arsem (3) found various amines, notably the aromatic amines, e.g., benzidine, *p*-toluidine, diphenylamine, *p*-phenylenediamine, metaphenylenediamine, and diisopropylamine, to be effective. In this case, linseed oil when heated with 1 per cent of benzidine reached the desired viscosity in 11¼ hours whereas without this compound under the same conditions better than 44 hours was required.

Auer and Susztek (6) consider oils as isocolloid systems and have on this basis found that the quantity of disperse phase can be increased by treating oils of the linseed type with polar compounds to

produce bodied oils. Generally speaking, these compounds are acidic inorganic and organic compounds, their salts, metallic and organic derivatives, the major portion being sulfonic acid derivatives. Auer (5) has also claimed variations in this treatment of increasing the disperse phase to include the use of metallic peroxides, weak alkalis (4), and alkaline earth metals and soaps. The quantity of these agents varies from 2 to 10 per cent. Incidentally some of the reagents used by Auer are identical with those previously claimed by Arsen.

Other reagents, as 0.2 to 1 per cent mercaptobenzothiosole or 0.1 to 0.5 per cent of diphenylguanidine, in the presence or absence of calcium resinate are claimed by Kozlov (34) to accelerate the thickening of oil, whereas these same agents retard the thickening in the presence of oleic or linseed fatty acids or various linoleates and resinates, as those of mercury, copper, barium, or strontium.

Sorensen and Konen (53) claim the use of aromatic compounds containing at least three condensed rings to shorten appreciably the bodying time of oils of the linseed type. Some of the reagents are derivatives of naphthoquinone, anthraquinone, anthracene, and phenanthrene. The amount of catalyst varies from 0.05 to 0.5 per cent.

Schwareman (49) claims the use of partially oxidized "phenanthrene-like" hydrocarbons to achieve the same end. In this instance ehrysene, retene, picene, etc., are oxidized to contain one or more ketone and/or hydroxyl groups.

Diaryl and dialkyl disulfides in amounts between 0.05 and 0.5 per cent were found by Parkin (40a) to increase substantially the bodying rate of oils.

The Northwestern Club (38) has studied the effect of rubber accelerators and numerous other compounds on the bodying rate of various oils.

A thickened oil suitable for use in lacquers, prepared by Pillnay (41), can also be made by heating tung oil with acetic acid and nitrosodiphenyl amine to 572° F. (300° C.) in the complete absence of air.

Caplan (11) has discovered that oils can be polymerized by treatment with dialkyl sulfates and phosphates, especially dimethyl sulfate, by heating at 221° F. (105° C.). Oils so treated are claimed to be desirable for varnishes.

According to Marcusson (37), a benzene solution of tung oil shaken with dilute nitric and sulfuric acids causes the beta eleostearine to precipitate out as a polymer. This is specific to tung oil.

A lubricating oil is made by decarboxylating oleic acid polymerized by the action of stannic chloride, according to Chowdbury, Chakraborty, and Majunder (12).

Various chlorides, e.g., titanium and silicon tetrachlorides, ferric chloride, and aluminum and zinc chlorides (19, 57), are used to thicken both tung oil and oils of the linseed type. Tung oil is much more sensitive to these agents than linseed oil. Accordingly, this difference has been made a basis for judging the purity of the former.

In order to prepare a cellulose ether varnish oil composition, miscible in the usual varnish solvents, Sherk and Peterson (51a) cook between 1 and 15 per cent of ethylcellulose with those oils ordinarily used in varnish making. The cellulose ether-polymerized drying oil composition shows good drying properties, low acidity, and forms varnish films considerably tougher than those formed from the usual type of heat-bodied oils.

It is generally accepted that oxidation is an important factor in oil polymerization; this is discussed in Chapter 4. It is therefore not considered as such in this chapter and accordingly only mere mention is made of a few oxidation processes.

It has been discovered by Heuck (25) that hydrogen peroxide in small quantities with some warming produces a thickened oil. A combination of heat-bodilying and blowing process is described by Schwarcman (50), in which case the oil acquires properties rendering it suitable for lacquer and varnish formulations.

Corkery (13a) in a series of patents, combines the heat-bodilying and blowing processes in various ways to produce quick-drying and good baking oils.

### COMBINED PROCESS

Usually the treatment of an oil with one of the chemical agents is combined with one of the physical processes, the most common being heating. Heating in any process is usually taken for granted. Therefore under this caption methods other than heating are considered.

A combination of a chemical and physical process is described by Auer (5) in which he coagulates an oil thickened by the presence of soap with X-radiation and ultraviolet rays.

### SEGREGATION OF POLYMERS OF HIGH MOLECULAR WEIGHT

Under this heading methods are considered which effect the removal of the polymerized portions of a stand oil from the unpolym-

merized portions. The latter comprises glycerides, with molecular weights not greater than 900, and the usual products of decomposition found in and produced in bodied oils. The separated polymerized portions show greatly improved properties, and because of this they serve as excellent tung oil substitutes.

*Selective precipitation* has been applied to bodied oils in several instances. Kotthoff (33) uses acetone as the extraction medium, in which case the solvent is mixed with the warm-bodied oil and permitted to cool. About 85 per cent of the original oil is recovered in an improved condition. Behr (8) has especially applied this idea to bodied fish and semi-drying oils. Solvents recommended are those of medium solvent power, such as alcohols of low molecular weight and ketones which will not dissolve compounds with molecular weights greater than 900. Table IV summarizes the results of a sardine oil treated according to this process.

TABLE IV  
EFFECT OF SELECTIVE PRECIPITATION ON BODIED OILS

	Original Oil	Heat-Bodied Oil	Settled Polymerized Oil	Non-drying Oil
Iodine value Wijs	201	112	118.3	100.9
Refractive index at 25° C.	1.4795	1.4883	1.4926	1.4872
Saponification value	190	190	185	197
Free fatty acid as oleic, %	0.2	1.56	0.28	3.8
Color (Lovibond)	35Y/2.5R	35Y/4.0R	35Y/4.0R	Greenish
Unsaponifiable, %	1	1	1	0.92
Viscosity *	A	X	Z <sub>5</sub> plus	G
Appearance	Clear	Cloudy	Clear	Cloudy
Ability to gel on heating	No	No	Yes	No
Drying	Fast, but tacky	Slow, and tacky	Fast	Non-drying
Surface	.....	.....	Hard	Non-drying
Water resistance	Poor	Poor	Excellent	Poor
Taste	Fishy	Burnt	Cooked	Tasteless
Odor	Fishy	Cooked	Odorless	Odorless

\* Gardner-Holdt Scale values.

Courtesy Otho M. Behr.

It is quite obvious that greatly improved drying properties result. More recently another type of vacuum purification or separation of oils has been introduced. This process is essentially one of *molec-*

ular evaporation.\* The compounds to be evaporated traverse only a very short distance in a vacuum such as is obtained in a cathode ray tube at temperatures in the neighborhood of 464 to 500° F. (240 to 260° C.). This process has been applied to the removal of vitamins from fish oils by Hickman (26). Waterman and Osterhof (62) and Fawcett and Walker (17) have applied this idea to the removal of products of low molecular weight in bodied oils. In this case these compounds represent acids and unpolymerized oil molecules, e.g., stearine and mixed fatty acid esters incapable of polymerization. The residue has greatly improved drying characteristics. In Table V the properties of the various fractions of a stand oil treated by this process are shown.

TABLE V (40)

PROPERTIES OF A BODIED OIL SUBJECTED TO MOLECULAR EVAPORATION

	Stand Oil	Residue	Distillate
Viscosity in poises	55.2	379.0	1.51
20°	1.4908	1.4957	1.4806
	0.9622	0.9756	0.9362
Acid number	7.3	1.5	19.4
Average mol. wt.	1610	3463	757

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## CHAPTER 3

### PRACTICAL HEAT-BODIED DRYING OILS AND PIGMENT-OIL PASTES

JOSEPH J. MATTIELLO

In Chapter 2 a thorough review of polymerization methods has been made; in this chapter practical heat-bodied drying oils are discussed. The oils considered are linseed, tung (Chinawood), oiticica, fish, and dehydrated castor oil. A discussion of the flow and livering characteristics of pigment pastes made with bodied linseed oils is also included.

#### Linseed Oil

**Raw Linseed Oil.** It contains a water-soluble mucilaginous substance of colloidal nature known as the "break." Unless this material is removed by refining, the oil is not fit for heat processing or for varnish making because the break coagulates and chars at high temperatures. Various refining methods are discussed in detail in Chapter 1 of Volume I; however, for the purpose of this chapter, a limited discussion of several refining methods is sufficient.

**Alkali-Refined Linseed Oil.** The higher grade of varnish oils is made by the alkali-refining process. Dilute caustic soda, in excess of the theoretical amount needed to neutralize the free fatty acid, is added to the raw linseed oil. Then the oil is washed with hot water until all the soap formed is removed. The break is also removed during neutralization. Now that the oil is free of the break and is practically neutral, it is bleached to a pale color with a combination of fuller's earth and activated carbon. The oil is then chilled to a low temperature to remove the vegetable waxes, and filtered. This complete process produces the highest grade of varnish oils—an alkali-refined, bleached, refrigerated varnish oil.

Since this oil is practically neutral, it can be bodied, heat-processed, at high temperatures to a heavy viscosity, and yet have a low acid



value and a light color. It is used in the manufacturing of lithographic and pale varnishes.

Figure 1 shows a diagrammatical flow sheet for producing an alkali-refined linseed oil. Other oils are produced by mechanically refining, by slightly oxidizing, or by adding metallic soaps to the raw oil to keep the break in suspension.

**Acid-Refined Linseed Oil.** The break is removed with sulfuric acid. This oil is mainly used to grind lead pigments. Because of the

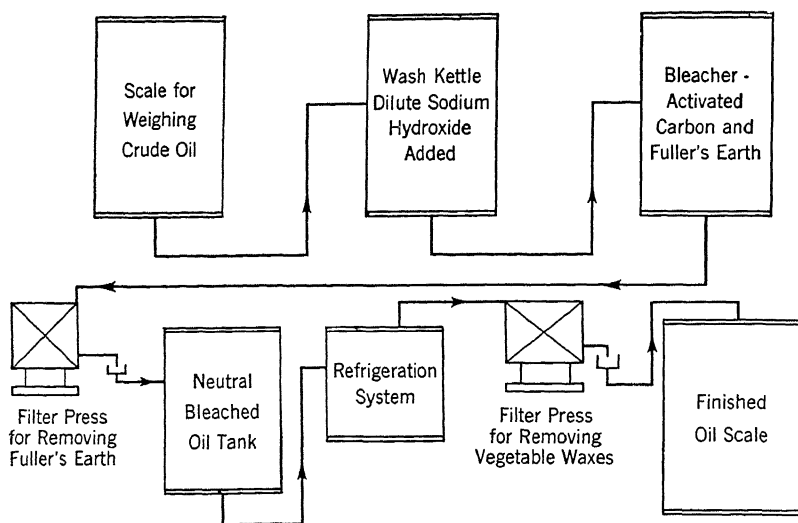


FIG. 1. Flow Sheet for Alkali-Refined Bleached Refrigerated Linseed Oil.

presence of sulfonic groups, which cannot be easily removed, this oil should not be used as a varnish oil, as it will darken at high temperatures.

**Oxidized Linseed Oil.** These oils are made by simply blowing air throughout the oil at low pressure and at elevated temperatures. In this way, the viscosity and the specific gravity are increased and the iodine number is decreased. An oil may be slightly oxidized or oxidized to sweetmeats by varying the time and conditions of blowing air.

The slightly oxidized oils are used in manufacturing dark-colored lithographic varnishes, patent-leather varnishes, and, generally, in dark-colored varnishes. Owing to this slight oxidation, the oil bodies

(increases in viscosity by means of heat) faster than the other refined oils.

Figure 2 shows the flow sheet for producing oxidized oils.

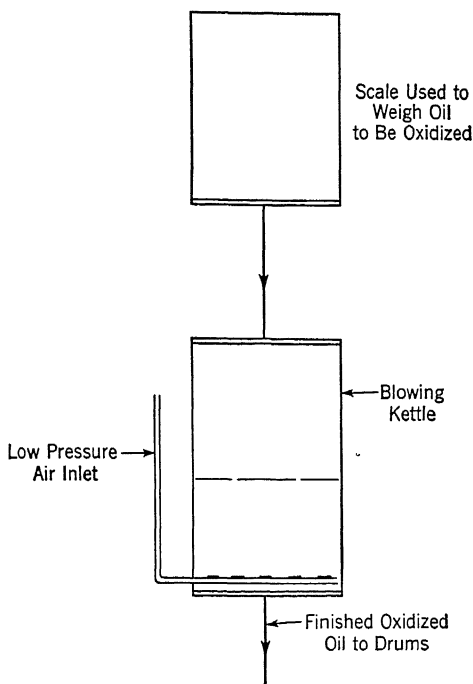


FIG. 2. Oxidized Oils.

### Heat-Bodied Drying Oils

The various methods and equipments employed in heat-bodily drying oils are described in Chapter 7, Volume III, Chapter 8, Volume III, and in the section on lithographic varnishes of Chapter 21, Volume III.

Heat-bodied linseed oil was first described as Standoil. A private communication from Karel Vettewinkel \* to the author of this chapter is herewith given to define and fix the origin of Standoil:

It seems that in the year 1837 mention was first made of a bodied linseed oil. It was produced by the application of heat and, if I am not mistaken, fired. This was an isolated case ascribed to a painter in a little Dutch village known as "Bennebroek." In the

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meantime linseed oil of increased viscosity was being produced mainly by exposing it to the sunlight. As you know, this is a very lengthy process. This all happened during the time when painters were expert in every phase of their trade and even went so far as to cook their own varnishes. In 1853, however, the first heavy-bodied linseed oil was made on a more or less commercial scale and was available for distribution to the trade. The man responsible for that was H. Vettewinkel Dzn., who was my great grandfather. He was the one who gave this material the name of "Standoil," with which he wanted to indicate that it was comparable to an oil which had been standing for a long time.

The first grade of Standoil made had a viscosity of from 60-70 poises comparable to G. H. Standard Z4. The acid number must have run around 20. With the advent of zinc oxide it was discovered that that type of Standoil would cause trouble and for that reason another grade was introduced. This latter material has a viscosity of from 35-40 poises and an acid number of from 12-18.

At present, both these grades are produced in Holland. The first is known as heavy Standoil or Standoil for white lead, while the second goes under the names of thin Standoil or Standoil for zinc oxide.

During the process of bodying drying oils from the raw state to that of heavy viscous liquids, many chemical and physical changes occur concurrently. Although the nature of these changes and all the factors that affect their velocity and sequence are not known, it is agreed that reactions of polymerization, condensation, cracking, oxidation, hydrolysis, rearrangement, and gelation are involved. The sequence of some of these reactions and other chemical changes are discussed in detail in Chapter 4 of Volume III. Here, we consider the rate of change of certain physical and chemical properties during processing; these properties are viscosity, specific gravity, color, apparent mean molecular weight, index of refraction, acid number, and iodine value. Practical properties such as the ease of wetting of bodied oils for pigments, drying, water and alkali resistance, permeability, toughness, and tackiness of the bodied oils are also considered.

The data discussed were obtained on samples taken from actual factory production batches of 250 gallons or more, processed at commercial temperatures.

In any discussion of the changes in properties during bodying, it must be remembered that the system is a complex one and that the results of this or of any single investigation must be influenced by local conditions (methods of heating, shape and material of kettle, effect of moisture formed by reactions or derived from air, and other

environmental conditions). Therefore, the properties of the original raw oil are given for each oil considered.

Two comparative studies have been made in the treatment of linseed oil:

1. Oil-bodied in air and oil-bodied under vacuum.
2. Oil-bodied in air and oil-bodied under carbon dioxide.

### Air-Bodied versus Vacuum-Bodied

Alkali-refined linseed oil was heat-bodied in commercial batches of 250 gallons in air and of approximately 600 gallons in vacuum at

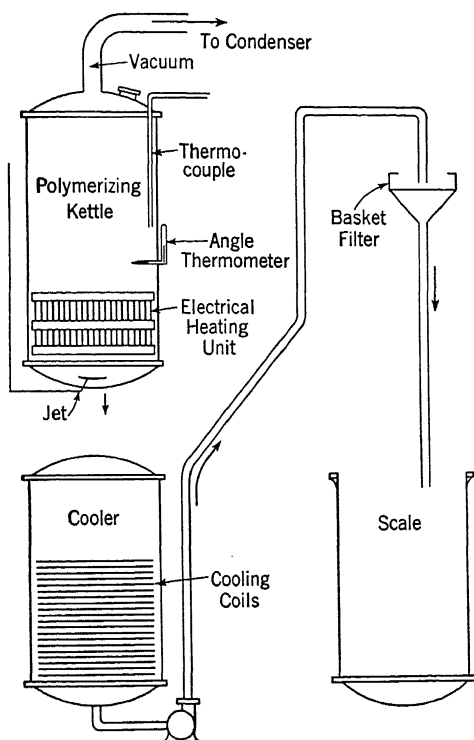


FIG. 3. Vacuum Polymerization Unit.

maximum temperatures of 535° F. (279° C.), 575° F. (302° C.), and 600° F. (316° C.) to a viscosity of 162 poises and higher. Figure 3 shows a vacuum polymerization unit. The alkali-refined linseed oil had the physical and chemical characteristics shown in Table I.

The properties of the air-bodied oil at three temperatures are given in Table II. Similar data for the vacuum-bodied oil are given in Table III.

TABLE I

## PROPERTIES OF ALKALI-REFINED LINSEED OIL

Color (20 mm.) Hess-Ives .....	82-65-75
Viscosity (poises) .....	0.232
Specific gravity .....	0.9327
Refractive index .....	1.4792
Ash .....	0.0003%
Acid number .....	0.28
Molecular weight .....	728
Iodine number .....	186.2
Thiocyanate number .....	114.7
Saponification number .....	191.8

The approximate analysis of the alkali-refined linseed oil used is:

Unsapnifiable .....	1.01%
Saturated acids .....	7.70%
Unsaturated acids:	
Linolenic acid .....	40.07%
Linoleic acid .....	42.50%
Oleic acid .....	9.79%

The methods of determining these properties are given in detail in the original paper (10).

### Physical and Chemical Properties

Since viscosity is a variable of great importance in the practical relation of oil to paint and since it also reveals one of the most obvious changes in oil upon heating, the changes of the other properties are plotted against viscosity. For convenience in comparing the data, the figures representing the oils processed in vacuum are shown alternately with those for the oils processed in air. The only exception is the figures for studying color change; and, in this case, the vacuum-bodied and air-bodied oils are shown in one figure, Fig. 4. The graphical representations are shown in Figs. 4 to 18.

Figure 4 indicates the development of color as the viscosity of the oil increases. Oils bodied in air developed more color than those bodied in vacuum. The higher the bodying temperature, the greater the color developed in oils bodied in both atmospheres. The cracking reactions which take place at the side and bottom of the kettle of the oils bodied in open air resulted in greater discoloration of oil. This

..BLE  
PHYSICAL AND CHEMICAL PROPERTIES OF ALKALI-REFINED LINSEED OIL BODIED IN AIR (7)

Temp.	Sample No.	Acid No.	Iodine No.	Viscosity Poises	Molecular Wt.	Specific Gravity	Refractive Index	Saponification No.	Hess-Ives Color	Gardner Color	Peroxide No.	Acetyl No.	% Insoluble Acetone
535° F. (270° C.)	*	0.28	186.2	0.23	738	0.9327	1.4792	191.8	82-65-75	3-4	2.1	3.0	0
	1	2.45	159.7	2.2	870	0.9461	1.4831	193.1	79-67-77	3-4	2.6	0.8	0
	2	3.00	154.3	3.3	1,055	0.9195	1.4841	193.5	81-66-73	3			6.5
	3	3.46	150.0	4.8	1,125	0.9528	1.4851	193.2	82-61-72	3-4	1.6	3.5	20.5
	4	4.27	143.9	10.1	1,290	0.9582	1.4866	193.6	77-60-70	4			37.5
	5	4.70	140.8	15.1	1,292	0.9609	1.4873	192.8	79-59-76	4-5	0.9	1.4	47.5
	6	5.25	138.0	34.2	1,370	0.9614	1.4881	193.5	81-51-69	5			59.5
	7	5.66	136.8	38.4	1,535	0.9663	1.4886	193.5	77-49-60	5-6	0.7	3.2	64.5
	8	6.01	134.5	36.0	1,670	0.9682	1.4892	193.6	77-46-61	5-6			67.0
	9	6.30	134.9	75.0	1,775	0.9694	1.4895	193.7	77-42-60	6	0.9	1.3	70.0
	10	7.05	133.7	115.0	1,890	0.9711	1.4901	193.3	74-39-58	6-7			71.5
	11	7.11	133.6	162.0	1,950	0.9715	1.4963	193.0	71-38-55	6-7	0.4	0.2	74.25
575° F. (302° C.)	*	0.81	180.5	0.58	771	0.9346	1.4850	193.8	84-65-83	3	2.1	1.4	0
	1	4.09	151.0	3.5	853	0.9508	1.4850	193.4	83-65-75	3	2.6		10.0
	2	5.13	146.0	5.9	908	0.9546	1.4850	193.5	82-60-75	3		0.0	21.0
	3	6.18	141.7	10.5	1,165	0.9591	1.48610	193.8	82-58-74	3-4	1.6		35.5
	4	6.65	139.8	13.9	1,293	0.9609	1.48690	193.3	83-58-71	4		0.0	51.0
	5	7.07	136.6	28.3	1,318	0.9650	1.48825	193.6	78-48-60	5			58.5
	6	8.02	136.0	32.9	1,390	0.9672	1.48890	193.6	78-42-61	5-6	1.5	0.0	62.5
	7	9.07	133.2	66.7	1,622	0.9701	1.4895	193.7	74-37-57	6			69.0
	8	10.27	133.5	96.7	1,648	0.9715	1.4905	193.4	64-31-59	6-7	0.3	0.0	69.5
	9	11.27	132.0	125.2	1,700	0.9722	1.4935	194.1	69-30-50	6-7			68.7
	10	12.00	132.0	257.0	1,798	0.9733	1.4980	192.9	53-19-34	7-8	0.0	0.0	70.7
600° F. (316° C.)	*	0.83	180.3	0.60	757	0.9342	1.4799	191.2	77-60-73	3	1.2	5.5	0
	1	5.25	142.8	4.1	926	0.9521	1.4844	191.2	73-60-69	3-4	1.8	6.2	15.0
	2	6.23	142.8	6.1	936	0.9551	1.4852	191.7	72-57-70	4		4.0	25.5
	3	7.00	139.3	6.10	1,073	0.9596	1.4866	192.3	77-52-62	5	0.9		35.0
	4	8.55	138.0	10.8	1,262	0.9610	1.4870	192.0	72-45-62	5-6		0.0	30.5
	5	10.7	133.9	13.6	1,261	0.9657	1.4882	192.7	63-40-51	6	1.1		51.0
	6	11.8	133.3	28.3	1,361	0.9677	1.4890	192.0	63-33-52	6-7	0.9		59.5
	7	13.75	131.7	63.8	1,415	0.9703	1.4896	194.6	60-24-44	7		1.4	69.0
	8	14.7	131.2	83.6	1,515	0.9719	1.4901	193.4	54-21-42	7-8	0.4	0.8	66.0
	9	15.3	132.1	94.6	1,525	0.9717	1.4904	193.9	54-21-35	8			66.0
	10	15.9	132.1	157.2	1,565	0.9740	1.4907	193.6	51-13-35	8-9	0.2	0.0	66.0

TABLE III  
PHYSICAL AND CHEMICAL PROPERTIES OF ALKALI-REFINED LINSEED OIL BODIED IN VACUUM (7)

Temp.	Sample No.	Acid No.	Iodine No.	Viscosity Pokes	Molecular Wt.	Specific Gravity	Refractive Index	Saponification No.	Hess-Ives Color	Gardner Color	Peroxide No.	Acetyl No.	% Insoluble Acetone
535° F. (279° C.)	*												
	1	0.28	186.2	0.23	738	0.4327	1.4702	191.8	82-85-75	3-4	1.5	5.3	0
	2	1.01	184.6	0.5	790	0.4320	1.4704	192.1	79-85-74	3	1.4	2.6	11.5
	3	1.03	152.6	3.9	980	0.4305	1.4705	191.8	82-89-78	1-2	1.1	5.8	28.0
	4	0.98	147.9	6.5	1,100	0.4549	1.4876	191.7	79-69-76	2-3	1.0	7.3	57.0
	5	0.95	142.8	13.5	1,235	0.4603	1.4870	191.7	80-68-72	2-3	1.0	8.7	66.0
	6	0.93	141.2	17.0	1,370	0.4616	1.4872	191.7	78-66-71	2-3	1.1	6.7	73.0
	7	0.94	138.9	31.0	1,460	0.4650	1.4882	191.7	79-63-68	2-3	1.0	9.0	75.2
	8	0.96	135.3	48.0	1,545	0.4672	1.4888	192.4	78-63-77	2-3	1.1	6.7	73.0
	9	0.76	135.9	114.2	1,800	0.4692	1.4893	191.7	78-60-68	3	0.6	5.2	80.0
	10	0.84	135.6	138.0	1,865	0.4706	1.4898	191.6	66-59-73	3	0.6	5.2	80.0
	11	1.12	134.5	268.0	2,145	0.4728	1.4904	192.4	78-57-68	3-4	0.6	5.2	80.0
575° F. (302° C.)	*												
	1	2.45	150.9	2.9	874	0.9485	1.4839	192.4	82-69-76	1-2	1.6	1.3	0
	2	3.03	143.6	5.8	1,158	0.9540	1.4853	192.2	80-83-71	2	0.3	4.4	0
	3	2.58	140.5	9.7	1,275	0.9585	1.4865	192.4	80-84-73	2	0.8	1.4	7.5
	4	2.41	138.9	12.9	1,303	0.9604	1.4869	191.9	77-64-78	2-3	0.8	0.0	28.0
	5	2.12	135.7	24.5	1,369	0.9652	1.4881	192.8	78-60-75	3	0.8	0.0	37.5
	6	2.09	133.5	40.7	1,543	0.9670	1.4890	192.1	82-61-74	3	0.1	4.7	56.5
	7	2.09	132.9	68.0	1,566	0.9691	1.4896	192.5	79-58-68	3-4	0.1	4.7	66.0
	8	1.70	130.5	114.0	1,703	0.9707	1.4903	191.1	76-55-63	4	0.0	4.9	77.0
	9	1.66	132.1	115.0	1,783	0.9711	1.4901	191.8	78-53-67	4	0.0	4.9	73.0
	10	1.39	133.4	150.0	1,805	0.9722	1.4901	191.0	77-55-68	4	0.0	5.2	80.0
	11	1.23	131.4	217.0	1,940	0.9726	1.4906	192.5	74-53-64	4	0.0	5.2	80.0
600° F. (316° C.)	*												
	1	0.38	184.0	0.5	705	0.9332	1.4706	193.6	75-67-74	2-3	2.3	5.7	0
	2	2.50	149.1	3.7	860	0.9506	1.4814	193.0	81-67-70	2-3	0.9	5.2	0
	3	2.44	143.1	6.6	1,065	0.9562	1.4846	193.4	78-66-76	2-3	1.0	5.2	10.0
	4	2.28	138.5	11.9	1,100	0.9622	1.4861	192.5	80-62-70	3-4	1.7	2.7	29.0
	5	2.23	133.6	14.3	1,382	0.9678	1.4877	192.5	79-58-71	3-4	1.7	2.7	44.0
	6	2.20	133.5	34.2	1,468	0.9658	1.4882	192.2	78-60-72	3-4	0.7	4.2	64.0
	7	2.23	132.1	57.3	1,492	0.9684	1.4890	192.9	76-59-69	3-4	0.7	4.2	70.5
	8	2.34	130.6	103.0	1,610	0.9693	1.4891	192.9	73-56-66	4-5	0.7	2.6	74.0
	9	2.30	130.0	142.0	1,665	0.9710	1.4903	192.9	70-48-66	5	0.7	2.6	75.5
	10	2.26	129.9	203.0	2,180	0.9714	1.4906	193.3	77-48-63	5-6	0.8	1.4	80.5
	11	2.22	130.1	278.0	2,230	0.9720	1.4910	193.4	60-47-63	5-6	0.8	1.4	80.0

\* Original oil.

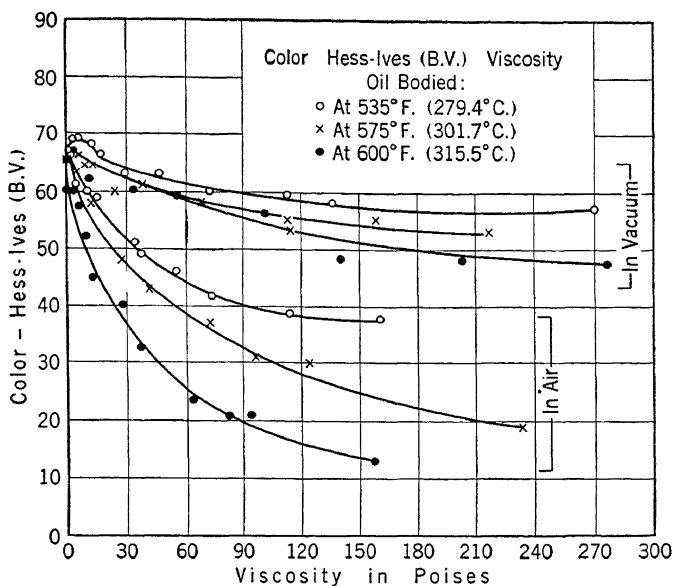


FIG. 4 (10).

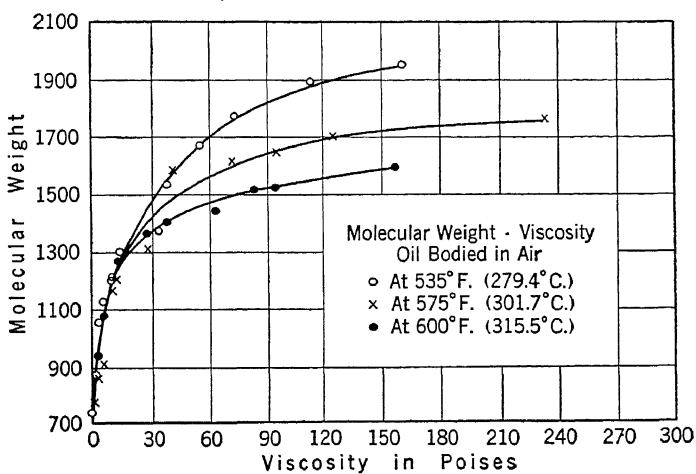


FIG. 5 (10).



is more evident as the bodying temperature increases. Some of the color-forming compounds developed during the bodying in vacuum were probably withdrawn.

The relation of molecular weight to viscosity is shown in Figs. 5 and 6. The increase in molecular weight is more rapid at first than the increase in viscosity, but with continued heating this condition is reversed. In the later stages of bodying a small increase in molecular

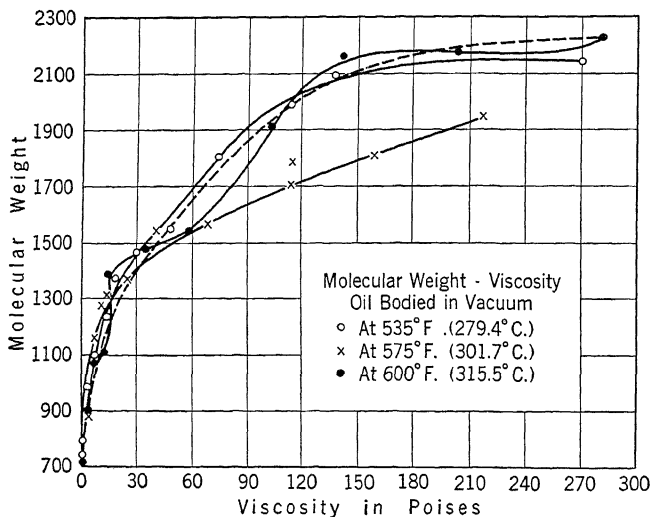


FIG. 6 (10).

weight is accompanied by a large increase in viscosity. In some cases, there is practically no increase in molecular weight with increased viscosity. This indicates that the polymerization reactions are slowing up and probably some sort of mechanical packing of the molecules is taking place which inhibits their free flow.

The specific gravity curves (Figs. 7 and 8) have identical form, regardless of the bodying temperature and the atmosphere. It is shown that there is a very large increase in specific gravity with a very small increase in viscosity during the early stages of bodying. Later there is an exceedingly small increase in specific gravity for a large increase in viscosity.

Figure 9 shows the relation of acid value to viscosity in oils bodied in air. It is shown that higher acidity is developed at the higher processing temperature. The curves in this figure do not illustrate anything new. The oils bodied in vacuum (Fig. 10) vary in acidity

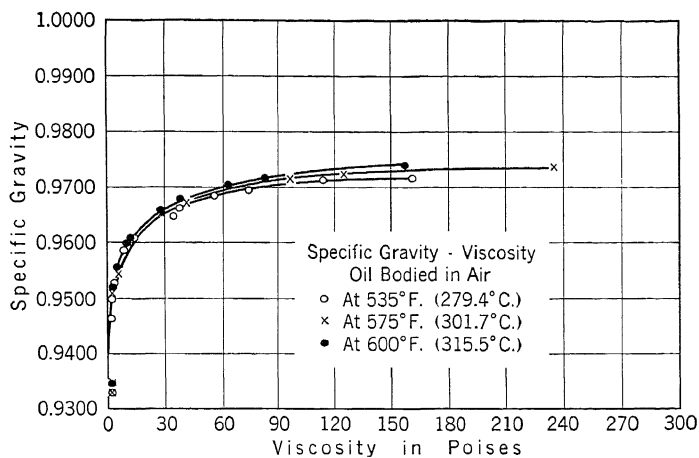


FIG. 7 (10).

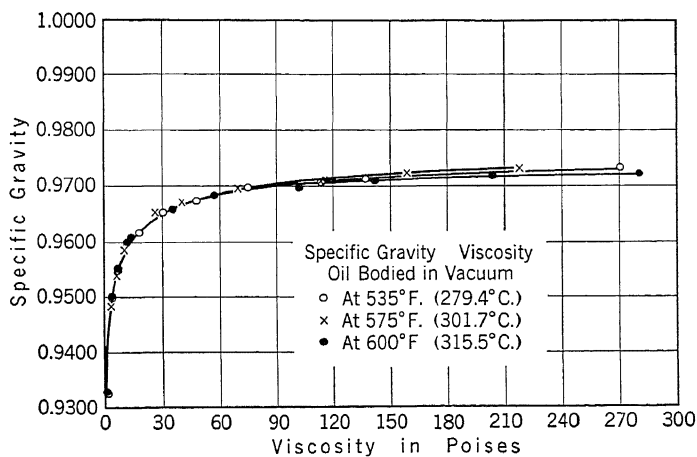


FIG. 8 (10).

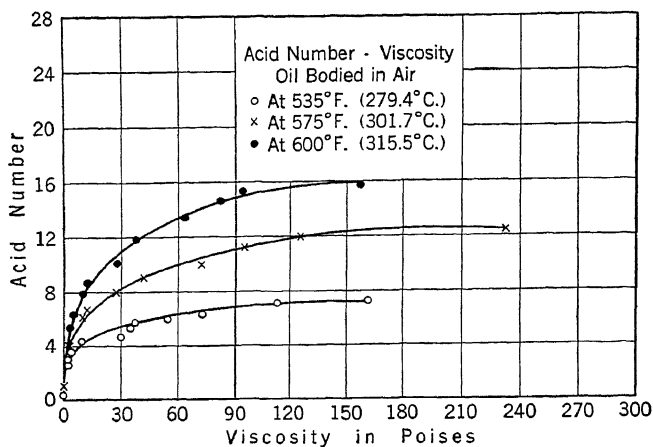


FIG. 9 (10).

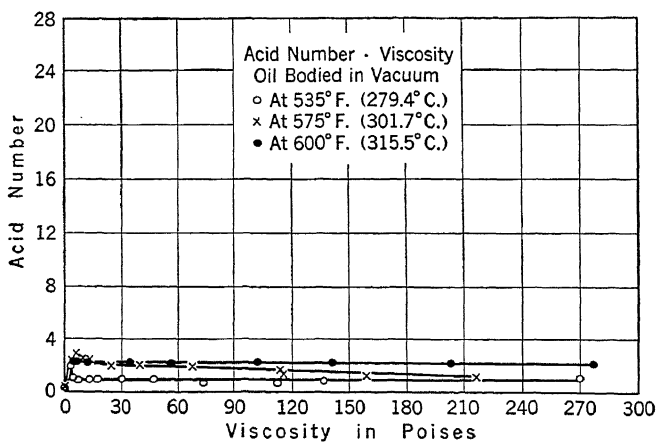


FIG. 10 (10).

within a value of one acid number for a variation in bodying temperature from 535° F. (279° C.) to 600° F. (316° C.). The acid value for any one bodying temperature is fairly constant. The acid number of the vacuum-treated oils is not a function of the cooking time. It is reasonable to assume that the acids are removed as soon as the glycerides are broken down.

Figures 11 and 12 show that there is a large increase in refractive index between the lower viscosity intervals, and but little change at

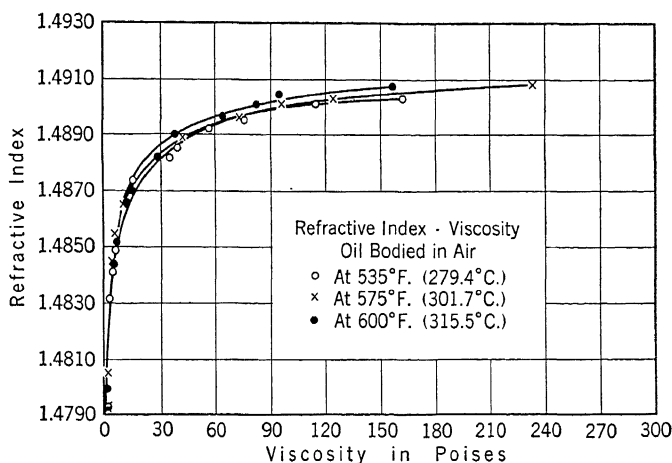


FIG. 11 (10).

high viscosities. The curves for each bodying temperature in both atmospheres have exactly the same character, and almost coincide with each other.

Iodine number in relation to viscosity is shown in Figs. 13 and 14. These figures indicate that, irrespective of the bodying temperature either in air or vacuum, the decrease in iodine number is from 180 to 150 units for an increase in viscosity from 0.23 to approximately 3 poises. Then, with an increase in viscosity of the bodied oil up to 270 poises, there is a decrease in iodine number to approximately 130 units. In other words, the greatest reduction in unsaturation takes place during the early stages of heat treatment. The iodine number-viscosity curves obtained from the oils processed in the two heating atmospheres are almost identical.

Saponification number in relation to viscosity is shown in Figs. 15 and 16. The saponification numbers for oils bodied in air remain

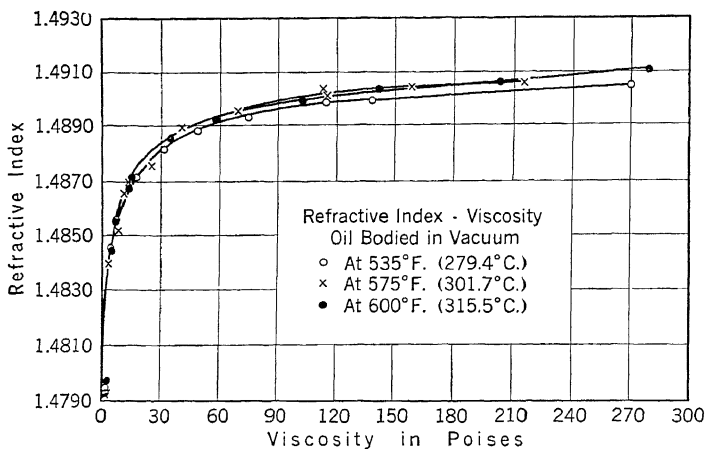


FIG. 12 (10).

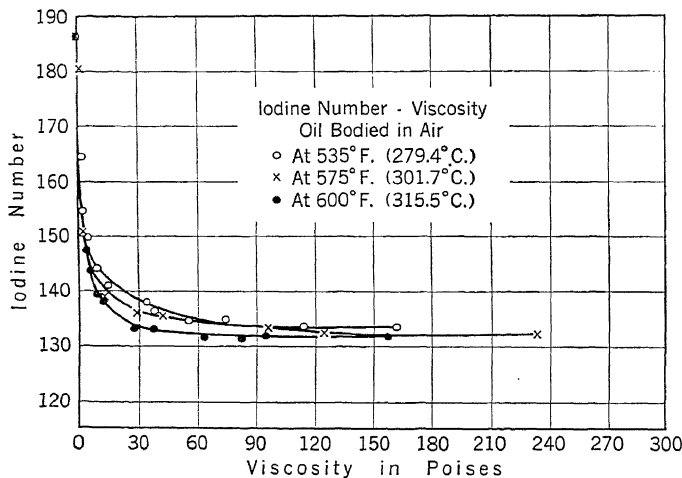


FIG. 13 (10).

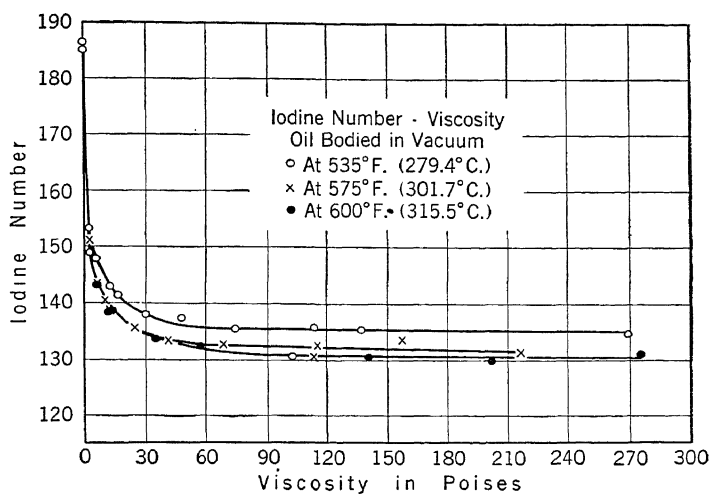


FIG. 14 (10).

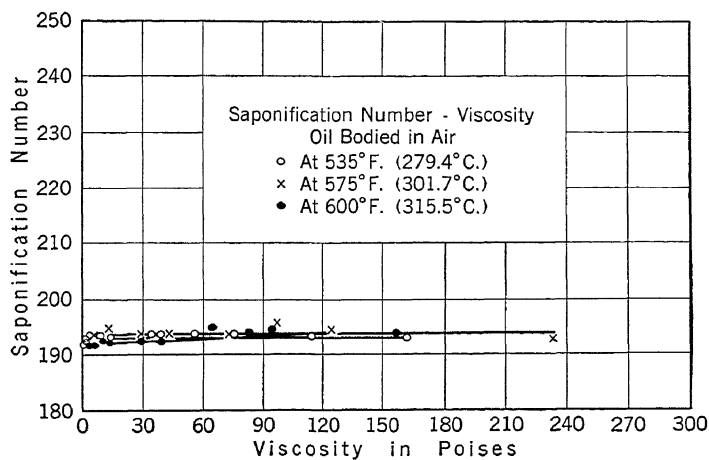


FIG. 15 (10).

practically constant; those of oils bodied in vacuum give an extremely slight slope to the curves; and the curves for the oils bodied at different temperatures are practically identical.

The percentage insoluble in acetone versus viscosity is shown in Figs. 17 and 18. The greatest increase in percentage insoluble in acetone (from 0 to approximately 45 per cent) takes place in the early stage of bodying as the oil increases in viscosity from 0.23 poises to approximately 8 poises. This applies to both bodying con-

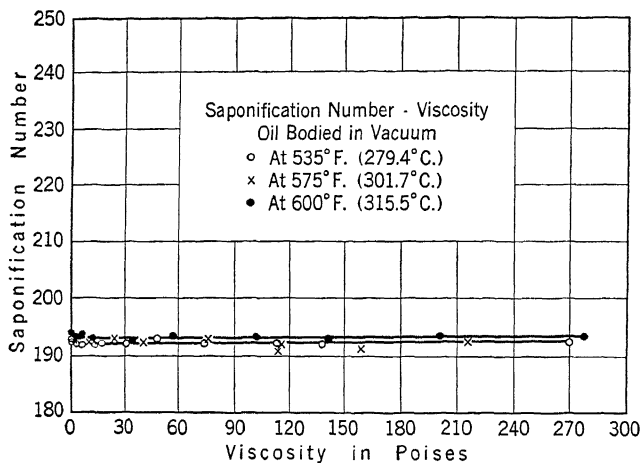


FIG. 16 (10).

ditions—air and vacuum. With a further increase in viscosity of the bodied oil up to 270 poises, the percentage of insoluble acetone increases to approximately 70–80 per cent. Another noteworthy point is that, at an oil viscosity of approximately 3 poises, a substance 20 per cent insoluble in acetone has been formed, indicating that at this point the reactions become colloidal in character. The rate of increase of the percentage insoluble in acetone is the same for oils bodied at 535° F. (279° C.) in either air or vacuum, whereas in the case of the oils bodied at 575° F. (302° C.) and 600° F. (316° C.) those processed in vacuum develop a higher percentage insoluble than those bodied in air. The higher acidity of the latter oils may disperse the gels and thus be responsible for the lower percentage insoluble in acetone.

Of the properties discussed, acidity and color are the only ones that can be used to differentiate between air- and vacuum-bodied oils. With an increase in viscosity from raw oil to bodied oil of 278 poises,

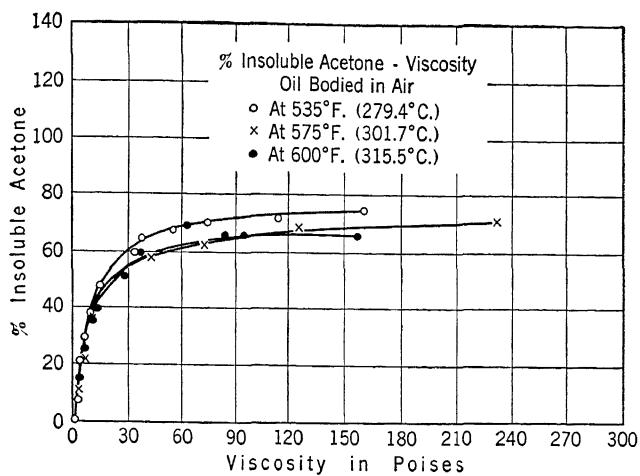


FIG. 17 (10).

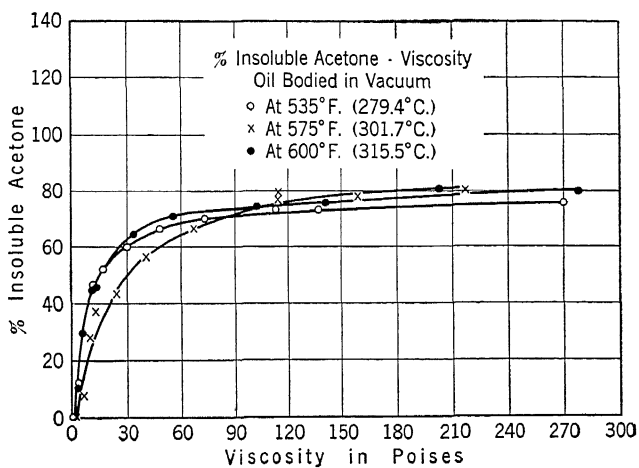


FIG. 18 (10).



a maximum acid number of only 2.2 is developed under the conditions of vacuum treatment and only then in the case of the highest bodying temperature. For the oils bodied in air, acid numbers of 7, 12, and 15 are developed for oils heated at 535° F. (279° C.), 575° F. (302° C.), and 600° F. (316° C.), respectively, and at viscosities of 162, 235, and 157 poises in the same order.

### **Air-Bodied Oil versus Oil Bodied in Carbon Dioxide**

In a comparative study of oil bodied in air versus oil bodied under carbon dioxide (7), the changes of the physical and chemical properties do not differ greatly from those shown for oil bodied in air and in vacuum, with the exception of the acid number. Greater acidity is developed under carbon dioxide than in air.

### **Flow and Livering of Pigment-Oil Pastes**

In this investigation, a study was made of flow (wetting) and livering characteristics of pigment-oil pastes made with peacock blue, zinc oxide, titanium oxide, and carbon blacks (long and short type) and bodied oils of varying viscosity, processed at three different temperatures.

### **Development of Pigment-Oil Pastes Data**

**Preparation of Pigment-Oil Pastes.** Peacock blue pastes were made using 20 grams of pigment and 20 grams of oil. Equivalent amounts by volume of zinc oxide (52.8 grams) and titanium oxide (30 grams) were used respectively, with the same weight of oil. For the carbon blacks it was found necessary to disregard this volume relationship. Therefore the carbon black pigment was decreased to that quantity which gave a paste of buttery consistency without changing the setting of the mill. It was found that 4 grams of carbon black to 20 grams of oil would give a paste of such consistency. Before grinding, all pigments except the blacks were heated for 2 hours at 212° F. (100° C.) and cooled in desiccators to remove any surface moisture. The black pigments were ground as received.

All pigments were incorporated in the bodied oils by grinding on a three-roller laboratory mill with a constant setting of the rolls which was measured by a metal strip of 0.0015 inch thickness. The pastes were passed through the mill five times.

**Properties of Pigments.** The pigments used had the following characteristics:

*Peacock Blue* \*

This is a lake which is made commercially by allowing solution of the dye (erio-glauceine) to be absorbed into a fine suspension of alumina hydrate, the excess dye being precipitated with barium chloride.

Specific gravity . . . . .	2.14 at 15.5° C.
Bulking value . . . . .	0.467 cc. per gram at 15.5° C.

*Florence White Seal Zinc Oxide* †

Diameter of the average particle . . . . .	0.26 micron (approx.)
Specific surface (square meters per gram of pigment)	3.2 meters (approx.)
Oil absorption (Gardner-Holdt method)	6.1 cc.
Specific gravity . . . . .	5.65 at 15.5° C.
Bulking value . . . . .	0.177 cc. per gram at 15.5° C.

*Titanium Dioxide* ‡

Diameter of the average particle . . . . .	0.3 micron (approx.)
Titanium Oxide Content (TiO <sub>2</sub> ) . . . . .	99% plus
Impurities	
Soluble salts	
Insoluble matter . . . . .	0.4%
Moisture	
Ferrous oxide (Fe <sub>2</sub> O <sub>3</sub> ) . . . . .	0.1%
pH . . . . .	7.0
Specific gravity . . . . .	3.88 at 15.5° C.
Bulking value . . . . .	0.258 cc. per gram at 15.5° C.

<i>Black Pigments</i> §	<i>Carbon</i>	<i>Black</i>
	<i>Long Type</i>	<i>Short Type</i>
Estimated particle size diameter in millimicrons . . . . .	50.70	40.60
Fixed carbon . . . . .	88.2%	95.1%
Total carbon . . . . .	92.8%	96.4%
Volatile . . . . .	11.8%	4.9%
Ultimate analysis of volatile O <sub>2</sub> (free or combined)	7%	3%
Hydrogen (H <sub>2</sub> ) combined or free . . . . .	0.2%	0.6%
Specific gravity . . . . .	1.75	1.75
Bulking value, cc. per gram . . . . .	0.571	0.571

The terms "long" and "short" are explained by Underwood (2) as follows:

"A 'short' carbon black pigment is one which when mixed with a large quantity of raw oil still remains stiff, and cannot be drawn out into a string between the fingers, but breaks.

"A 'long' carbon black pigment when mixed as above can be drawn into a string between the fingers."

Both of the carbon blacks used in this work were made from natural gas.

\* Values given by F. H. Levey & Company.

† Values given by the New Jersey Zinc Company.

‡ Values given by the R. T. Vanderbilt Company.

§ Values given by Binney & Smith Company.

### Flow of Paste

The Binney-Smith Flowmeter (Fig. 19), which measures the flow of pastes on an inclined plane, was used to determine the flow charac-

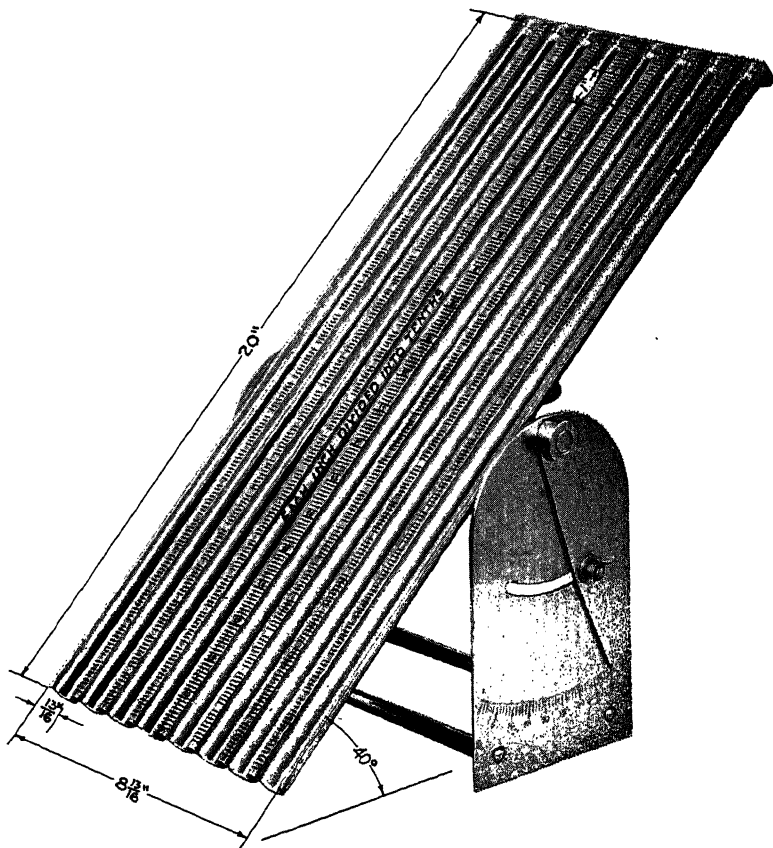


FIG. 19. Binney and Smith Flowmeter.

teristics. This apparatus consists of seven semicircular metal tubes with two side lips for each tube, all screwed together to form a table ( $20 \times 8\frac{1}{8}$  inches) with seven parallel grooves, each with a lip graduated from 0 to 20 inches in tenths of inches. At the starting point, a metal strip ( $1 \times 8\frac{1}{8}$  inches) is screwed along the ends; this strip projects  $\frac{1}{8}$  inch above the surface of the instrument, to enable the operator to scrape from his knife the material being tested. The angle

of the instrument to the horizontal is controlled by an adjusting screw in conjunction with a steel scale which is calibrated in degrees.

The flow measurements were made at a temperature of 60° F. (15.6° C.) one hour after grinding the paste and with the Flowmeter table tilted at an angle of 40°. Equal volumes of all the pastes were examined. This was accomplished by the use of a cylindrical metal cup whose capacity is 2.4 cc.

The flow characteristics are defined as:

Very excellent flow (VEF)	Flows 8.5+ inches in 20 minutes.
Excellent flow (EF)	Flows 8.5-7 inches in 20 minutes.
Very good flow (VGF)	Flows 7-5.5 inches in 20 minutes.
Good flow (GF)	Flows 5.5-3 inches in 20 minutes.
Fair flow (FF)	Flows 3-1 inches in 20 minutes.
Poor flow (PF)	Flows 1-0 inch in 20 minutes.

### Peacock Blue Pastes

**Oils Bodied in Air.** The flow and livering characteristics of peacock blue pastes, made with bodied oils which were processed at several different temperatures in air, are shown graphically in Figs. 20 and 21.

In Fig. 20, the maximum processing temperatures are plotted against the viscosity of the bodied oil for the various flow characteristics of the pigment-oil pastes. The straight lines show the range of viscosities for each flow characteristic. The figure shows that overlapping exists for several flow characteristics, particularly with the batches processed at 535° F. (279° C.) and 625° F. (329.5° C.). At each of these temperatures two batches of oil were processed, and in plotting the flow characteristics the extreme oil viscosities of each type of

TABLE IV

SHOWING HOW POINTS FOR FIG. 20 WERE OBTAINED FOR OILS BODIED AT 625° F. (329.5° C.) (7)

Character of Paste When Ground	Oil Viscosity in Poises	Oil Viscosity in Poises	Viscosity Range Used in Plotting in Poises, Fig. 20
EF	3.7-20.2	2.75-16.6	2.75-20.2
FF	36.8-46.3	60.0 -63.4	36.8 -63.4

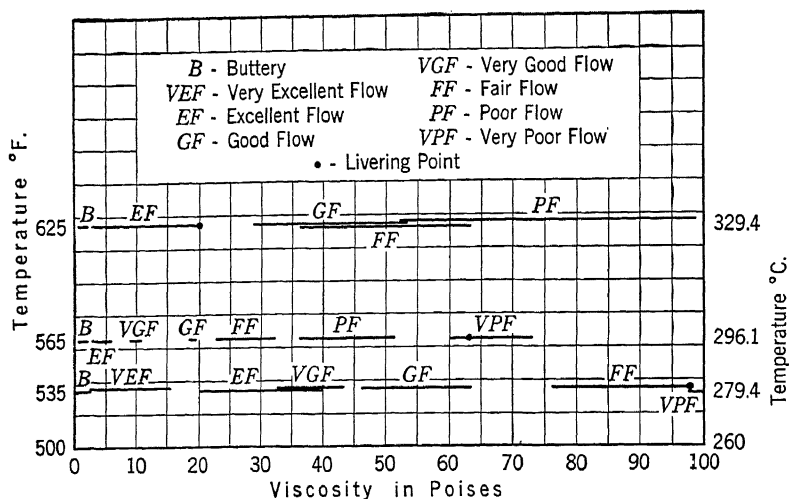


FIG. 20. Maximum Bodying Temperature—Viscosity.

Flow and living characteristics of peacock blue pastes made with bodied linseed oils processed in air (7).

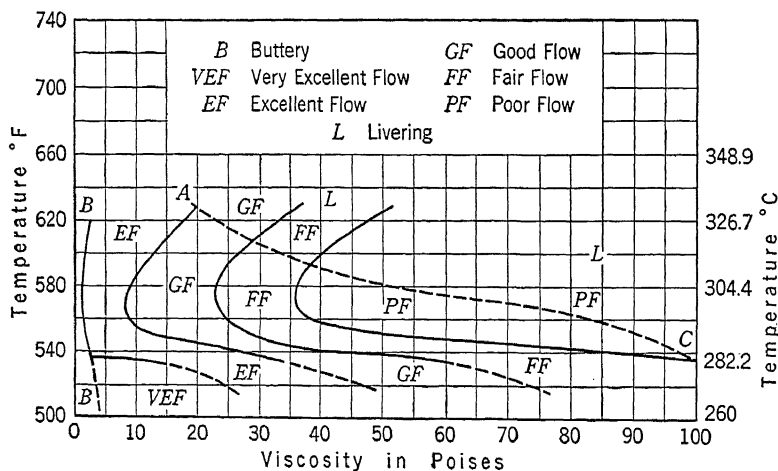


FIG. 21. Maximum Bodying Temperature—Viscosity.

Flow and living characteristics of peacock blue pastes made with bodied linseed oils processed in air (7).

flow are given. Table IV illustrates the viscosity values used in Fig. 20 for two batches bodied at 625° F. (329.5° C.).

The line chart data (Fig. 20) for each temperature were used to make the regional diagram (Fig. 21) by drawing the appropriate boundaries. By means of solid lines, areas are shown for each specific flow characteristic of the pigment-oil pastes. It is to be noted that as the viscosity of the bodied oils increases, first pastes are of buttery consistency, then of excellent flow, good flow, fair flow, and poor flow. It will be shown that all pigments do not exhibit the same number nor the same order of change of flow characteristics. For example, peacock blue pastes develop the most specific flow characteristics and the black pastes the least.

Although it is shown in Fig. 21 that a line divides one flow area from another, further study should change this line into a band because under no condition does the wetting of an oil for a pigment change abruptly within a narrow viscosity range as indicated by a line. In other words, for very small increases in viscosity of two bodied oils, at any point of a line, it is not possible to get a pigment-oil paste of excellent flow on the one side of the line and a paste of good flow on the other side. There must exist a transition stage for passing from one type of flow to another.

**Livering.** The development of the livering area which is above the curve *A-C* in Fig. 21 is of considerable practical importance. Although this subject is discussed in greater detail in Chapter 8, Volume IV, it is discussed here sufficiently for the present purpose.

Livering is the term applied to a state of fixed rigidity of a pigment-oil paste which results from a drastic change in consistency upon aging. This change may be of such magnitude that materials of excellent flow, good flow, or poor flow may alter to a rigid state. The term "livering" is used because of the resemblance of the resulting product to a piece of liver. The phenomenon of livering is the result of an irreversible reaction. It is most pronounced with reactive pigments like zinc oxide, alumina lakes, and red lead.

The accelerated livering method of Mattiello and Work (7) was used to develop the data to plot curve *A-C*. In this method, a pigment-oil paste is placed in a capsule and covered, and the capsule is placed in an oven maintained at 180° F. The paste is examined at the end of 24, 48, and the limiting time of 72 hours. It has been shown (8) that a pigment oil-paste which does not liver in the limiting time of 72 hours at 180° F. will not liver on aging.

This property of livering is of practical importance because those bodied oils, and other vehicles which have livering tendencies, affect the packaging characteristics, owing to their instability, evident by the increasing consistency of a pigmented product on standing.

**Oils Bodied in Carbon Dioxide.** Figure 22 shows the flow area for peacock blue pastes made with bodied oils, processed at various temperatures under carbon dioxide. There are only three areas de-

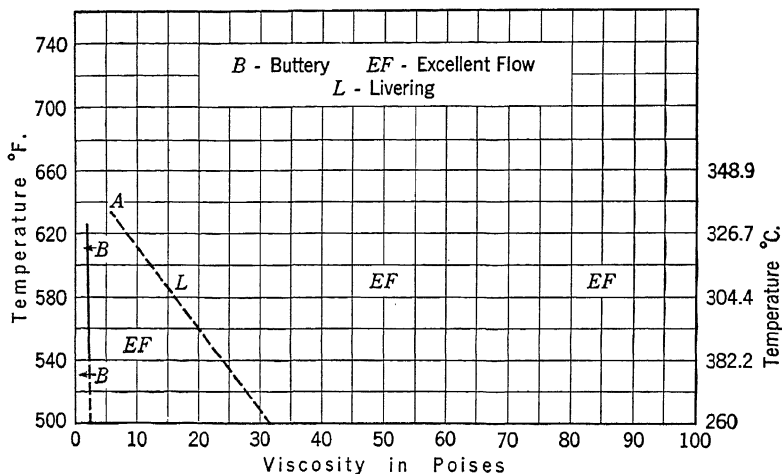


FIG. 22. Maximum Bodying Temperature—Viscosity.

Flow and livering characteristics of peacock blue pastes made with bodied linseed oils processed in an atmosphere of carbon dioxide (7).

veloped in this figure, compared with six for peacock blue paste (Fig. 21) made with oils bodied in air. These are the areas of buttery consistency, excellent flow, and livering. The large excellent flow area is probably due to the higher acidity of oil bodied under carbon dioxide. The Baltimore Paint and Varnish Production Club (1) has shown that when the carbon dioxide is blanketed only over the surface of the oil and, in addition a partial vacuum is employed, the oils bodied in this system have less livering tendency than when the carbon dioxide is bubbled from the bottom of the kettle. The oils bodied in vacuum have, for all practical purposes, either no livering tendency or a slight tendency to liver.

### Zinc Oxide Paste

The zinc oxide pastes were made by grinding 52.8 grams of pigment with 20 grams of the bodied linseed oil.

**Oils Bodied in Air.** Figure 23 shows graphically the flow areas as developed for zinc oxide oil pastes; here there are four areas—buttery, excellent flow, good flow, and fair flow. The superimposed livering curve indicates that most of the pastes in the good flow region and all in the fair flow regions will liver.

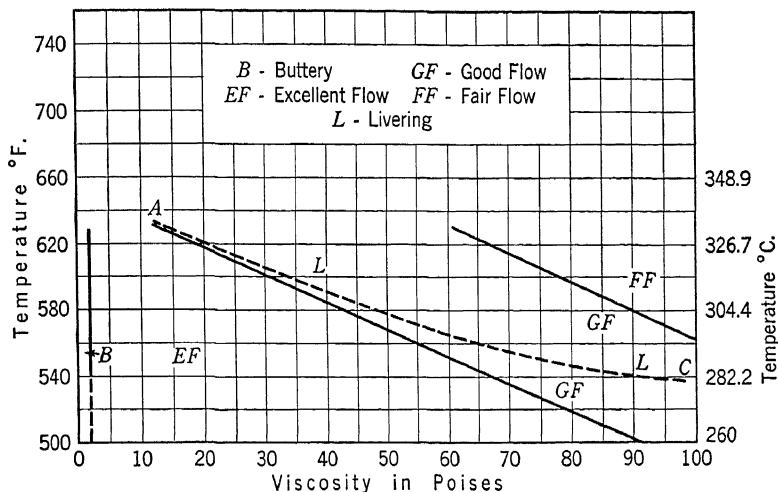


FIG. 23. Maximum Bodying Temperature—Viscosity.

Flow and livering characteristics of zinc oxide pastes made with bodied linseed oil processed in air (7).

**Oils Bodied in Carbon Dioxide.** Figure 24 shows that, in this case, there are only three flow areas. The region of excellent flow is considerably broader for the high temperature oil than for the corresponding oil bodied in air. However, most of the pastes having excellent flow will liver.

### Titanium Oxide Pastes

Titanium oxide pastes were made by grinding 30 grams of pigment with 20 grams of bodied linseed oil of various viscosities.

**Oils Bodied in Air.** Figure 25 shows graphically that four areas are developed for titanium pigment-oil pastes. They are buttery consistency, excellent flow, good flow, and fair flow areas. It is to be noted that no livering area is developed with titanium oxide pastes. This is also true for paste made with oil bodied in carbon dioxide.



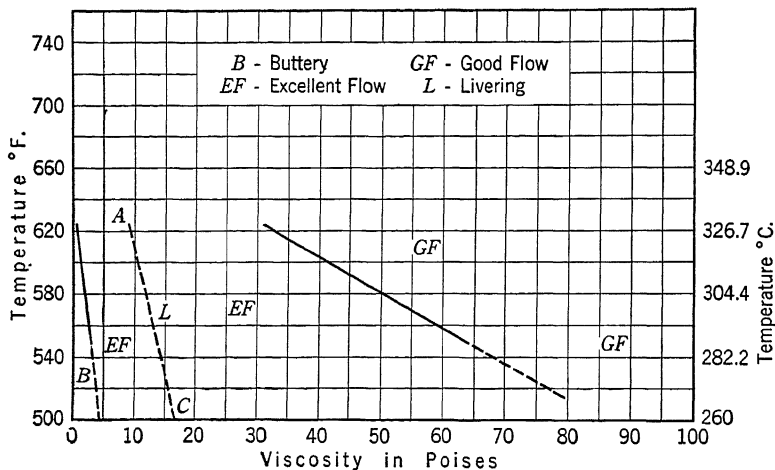


FIG. 24. Maximum Bodying Temperature—Viscosity.

Flow and livering characteristics of zinc oxide pastes made with bodied linseed oils processed in an atmosphere of carbon dioxide (7).

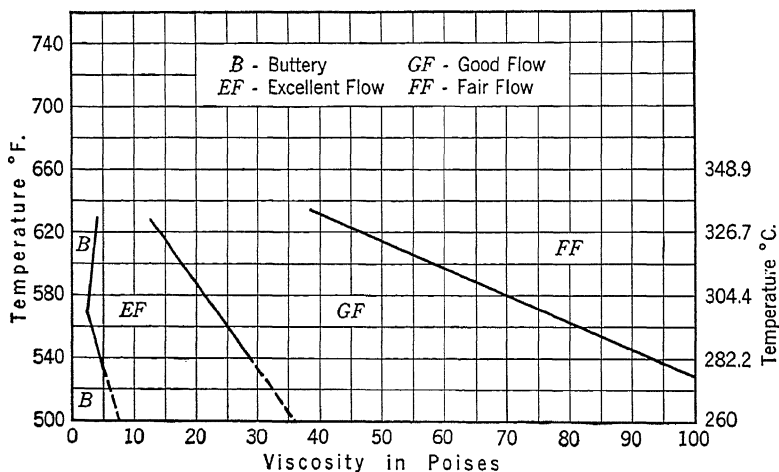


FIG. 25. Maximum Bodying Temperature—Viscosity.

Flow characteristics of titanium oxide pastes made with bodied linseed oils processed in air (7).

### Carbon Black Pastes

As previously stated, a radical departure from the pigment volume to oil volume ratio used in the preparation of the pastes for the other pigments was necessary in the grinding of the carbon black pigments because of the decidedly poorer wetting ability of these pigments. A volume of carbon black was used just sufficient to produce a buttery consistency paste. The final composition of such pastes was, both for the long type and short type of carbon black, 4 grams of black pigment to 20 grams of oil.

**Oils Bodied in Air.** Figure 26 shows the areas of each flow characteristic for the long type carbon black pastes made with oils bodied at temperatures from 535° F. to 625° F. (279.4° C. to 329.5° C.) It is important to note that with the increasing viscosity of the bodied oils, the flow areas change from buttery to poor flow to fair flow and finally to good flow. The order of flow characteristics obtained with the black pigments is the reverse of that obtained with peacock blue, zinc oxide, and titanium oxide.

The important points illustrated in Fig. 26 are:

1. The bodied oils processed at higher temperatures disperse the long type carbon black pigment decidedly better than oils processed at lower temperatures. A paste of good flow is obtained with a high temperature oil (625° F.) at a viscosity of 12.5 poises while with a low temperature oil (535° F.) good flow does not occur until a viscosity of 47 poises is reached.
2. The ranges from buttery through poor flow and fair flow are decidedly shorter for the high temperature oils than for the low temperature oils.
3. The buttery area occurs in a wider viscosity range at the lower processing temperatures which again indicates that the high temperature bodied oils disperse the long type carbon black more readily than do the low temperature bodied oils.
4. The good flow area is relatively large and range increases as the temperature rises, again indicating that the higher temperature bodied oils disperse the long type carbon black more readily than the oils heat-bodied at low temperatures.

Figure 27 shows the areas of each flow characteristic for the short type carbon black pastes made with oils bodied at temperatures of 535° F. (279.4° C.) to 625° F. (329.5° C.). The areas of the flow characteristics are the buttery area, poor flow, fair flow, and good

flow. In this particular instance, the area of poor flow is empirically divided into two areas, one of poor flow for the high temperature bodied oils and the other of very poor flow for the low temperature bodied oils.

An examination of Figs. 26 and 27 show that the buttery and the poor flow areas of the long type carbon blacks are smaller than those developed by the short type carbon blacks. The good flow area of

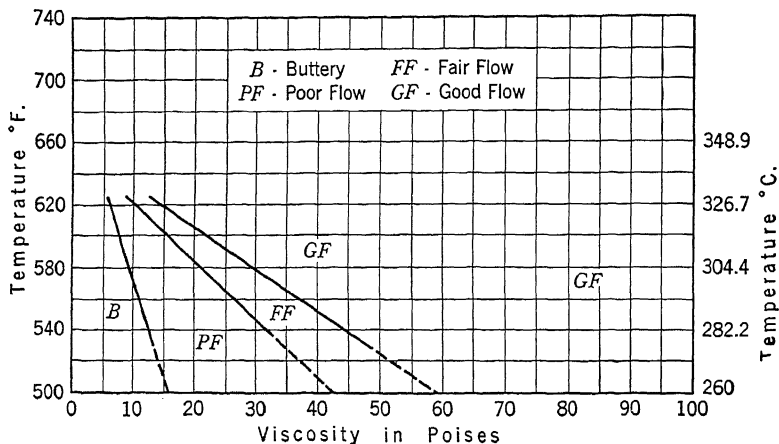


FIG. 26. Maximum Bodying Temperature—Viscosity.

Flow characteristics of carbon long-type black pastes made with bodied linseed oils processed in air (7).

the long type carbon blacks is considerably larger than the same area of the short type carbon black. The good flow area for the long type carbon black begins to develop for the high temperature 625° F. (329.5° C.) oil at a viscosity of 12 poises, and for oil bodied at 535° F. (279.4° C.) good flow begins at a viscosity of 47 poises. The good flow area of the short type carbon black does not develop until the bodied oil has reached a viscosity of approximately 100 poises for oils bodied at 625° F. (329.5° C.) whereas for oils bodied at 535° F. (279.4° C.) and at the same viscosity (100 poises) or higher only fair flow pastes are obtained. These results indicate that the long type carbon black is an easier pigment to wet than the short type carbon black.

**Order of Diminishing Wettability of Oil for Pigments.** Judged from the viscosities of the bodied oils of the pastes which just change from buttery consistency to either very excellent or excellent flow,

the pigments studied fall, in general, in the following order of diminishing ability of the bodied oil to wet the pigments:

1. Zinc oxide.
2. Peacock blue.
3. Titanium oxide.
4. Carbon black—long type.
5. Carbon black—short type.

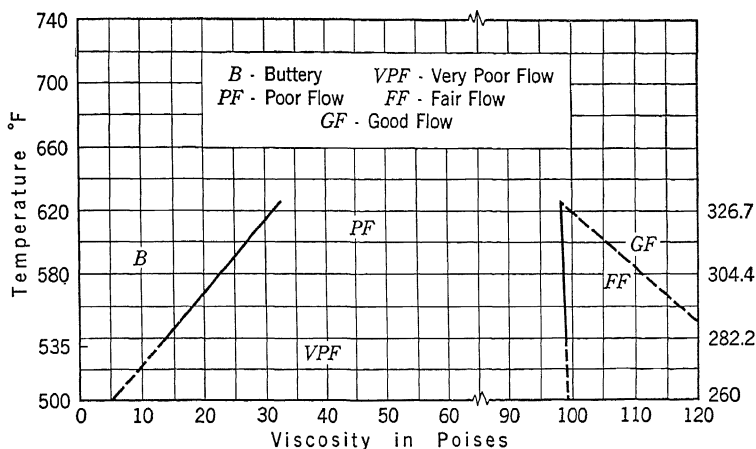


Fig. 27. Maximum Bodying Temperature—Viscosity.

Flow characteristics of carbon short-type black pastes made with bodied linseed oils processed in air (7).

**Other Improved Properties.** A bodied oil in comparison with raw oil is also improved considerably in its ability to dry more quickly, better resistance to water and to alkali, increased impermeability to moisture, and in ability to wet pigments easily. A bodied oil has less tendency to penetrate and therefore produces a dried film of higher luster. A bodied oil has better binding properties for pigments; on the other hand, when used in pigmented products (paints and enamels), a bodied oil induces hard brushing because of its increased tack.

### Tung and Oiticica Oil

**Tung oil** is used in the bodied state, not only in varnishes for the paint industry but also in varnishes for the ink industry and for the linoleum industry. Table V gives the changes in the physical and chemical properties of tung oil as a function of time during heat bodying, on a commercial scale (250 gallons) in air at 450° F.

## 74 HEAT-BODIED DRYING OILS AND PIGMENT-OIL PASTES

(232.2° C.). The properties of the original raw tung oil used in this particular investigation are:

PROPERTIES	TUNG OIL
Specific gravity .....	0.9392
Refractive index .....	1.5163
Acid number .....	6.4
Molecular weight .....	635
Saponification number .....	196
Gelation time at 540° F., min.	9.75

TABLE V

## PHYSICAL AND CHEMICAL PROPERTIES OF OILS (12)

Time	Elapsed Time <i>Hr. Min.</i>	Sample No.	Viscosity <i>Poises</i>	Mol. Weight	Acid No.	Gard- ner Color	Sp. Gr. 20.6±0.2° C.	Refrac- tive Index	Saponifi- cation No.
Tung Oil Heat-Bodied at 450° F. in Air									
8:50 A.M.	0 0	1 (raw)	2.28	635	6.4	4	0.9391	1.5163	196.1
9:48	0 58	2	2.29	642	6.7	4	0.9392	1.5163	204.6
10:03	1 13	3	2.41	660	6.6	4	0.9393	1.5161	
10:18	1 28	4	2.45	679	6.5	4	0.9394	1.5160	
10:33	1 43	5	2.86	694	6.5	4	0.9406	1.5152	210.7
10:48	1 58	6	3.93	726	6.6	4-	0.9435	1.5138	
11:03	2 13	7	6.44	780	6.5	4-	0.9449	1.5129	
11:13	2 23	8	9.42	830	6.5	4-	0.9498	1.5120	
11:23	2 33	9	14.6	920	6.6	4-	0.9522	1.5111	
11:33	2 43	10	22.6	992	6.8	3+	0.9545	1.5105	
11:43	2 53	11	38.5	1,050	6.6	3+	0.9573	1.5101	
11:53	3 3	12	65.6	1,091	6.4	3+	0.9586	1.5093	
12:03 P.M.	3 13	13	125	1,110	6.4	3+	0.9608	1.5090	
12:13	3 23	14	345	1,632	6.6	3+	0.9618	1.5082	

The data of Table V are shown in graphical form in Fig. 28. It is interesting to note that the viscosity, molecular weight, specific gravity and refractive index do not show any change until the oil approaches the processing temperature of 450° F. (232.2° C.). The acid number does not appear to increase a great deal during the whole processing period. At the end of the processing period, the viscosity of tung oil rises very sharply for a very short increment increase of heating time.

Oiticica oil is similar to tung oil in its practical bodying properties under the influence of heat. In Table VI is given the change of the physical and chemical properties as a function of time during the processing of oiticica oil on a commercial scale (250 gallons) in air

TABLE VI  
PHYSICAL AND CHEMICAL PROPERTIES OF OILS (12)

Time	Elapsed Time <i>Hr. Min.</i>	Sample No.	Viscosity <i>Poises</i>	Mol. Weight	Acid No.	Gardner Color	Sp. Gr. 20.6±0.2° C.	Refractive Index	Saponifi- cation No.
Oiticica Oil Heat-Bodied at 490° F. (254.4° C.) in Air									
10:03 A.M.	0 0	1 (raw)	Semisolid	695	4.9	4+	0.9752	1.5139	192.1
12:16 P.M.	2 13	2	Semisolid	705	5.3	4+	0.9732	1.5140	197.9
12:26	2 23	3	Semisolid	710	5.9	4+	0.9759	1.5140	...
12:36	2 33	4	Semisolid	725	4.6	4+	0.9730	1.5145	192.3
12:46	2 43	5	Semisolid	748	4.9	4+	0.9749	1.5140	...
12:56	2 53	6	7.47	780	5.1	4+	0.9750	1.5140	198.0
1:06	3 3	7	12.8	830	5.9	3+	....	1.5120	...
1:12	3 9	8	21.4	905	6.4	3+	0.9830	1.5110	...
1:17	3 14	9	32.2	1,000	6.6	3½	0.9859	1.5100	...
1:22	3 19	10	53.6	1,080	6.7	4-	0.9860	1.5090	...
1:27	3 24	11	89.4	1,210	7.2	4-	0.9908	1.5080	...
1:32	3 29	12	144.2	1,355	7.5	4	0.9938	1.5075	...
1:55	3 51	13	358	1,605	8.0	4+	....	1.5050	...

Oiticica Oil Heat-Bodied at 450° F. (232.2° C.) in Air									
9:06 A.M.	0 0	1 (raw)	Semisolid	685	5.3	5½	0.9726	1.5140	191.8
11:08	2 2	2	Semisolid	743	5.7	5½	0.9729	1.5140	196.9
11:23	2 17	3	Semisolid	778	5.5	5½	0.9731	1.5139	...
11:38	2 32	4	Semisolid	795	5.8	5+	0.9734	1.5140	...
11:53	2 47	5	Semisolid	803	6.0	5+	0.9741	1.5135	...
12:08 P.M.	3 2	6	9.7	817	6.6	5+	0.9786	1.5130	...
12:23	3 17	7	16.1	843	7.2	5-	0.9826	1.5114	...
12:33	3 27	8	23.4	873	7.6	5-	0.9842	1.5108	...
12:43	3 37	9	35.4	1,035	8.0	4½	0.9859	1.5101	...
12:53	3 47	10	54.5	1,105	8.3	4½	0.9889	1.5094	...
1:03	3 57	11	80.3	1,225	8.3	4½	0.9902	1.5088	193.2
1:13	4 7	12	118.4	1,395	8.8	4½	0.9922	1.5081	...
1:23	4 17	13	168	1,455	8.9	4½	0.9933	1.5081	198.0
1:33	4 27	14	238	1,525	9.0	4½	0.9941	1.5080	...

Oiticica Oil Electrically Heat-Bodied at 450° F. (232.2° C.) in CO <sub>2</sub>									
8:45 A.M.	0 0	1 (raw)	5.23	668	5.2	5+	0.9718	1.5141	...
9:36	0 51	2	5.48	691	5.2	5+	0.9719	1.5139	...
9:51	1 6	3	5.27	729	5.2	5	0.9723	1.5138	...
10:06	1 21	4	6.28	741	5.4	5	0.9725	1.5140	...
10:21	1 36	5	6.92	763	5.6	5-	0.9737	1.5137	...
10:36	1 51	6	8.34	837	5.9	4+	0.9748	1.5132	...
10:51	2 6	7	10.9	876	6.2	4-	0.9772	1.5125	...
11:06	2 21	8	15.9	891	6.5	3½	0.9795	1.5115	...
11:16	2 31	9	21.1	906	6.8	3½	0.9817	1.5107	...
11:28	2 43	10	32.4	968	7.4	3½	0.9842	1.5100	...
11:40	2 55	11	45.3	1,052	7.6	3½	0.9865	1.5095	...
11:50	3 5	12	70.1	1,080	7.8	3½	0.9883	1.5089	...
12:00 P.M.	3 15	13	92.5	1,125	8.1	3+	0.9898	1.5084	...
12:05	3 20	14	120	1,225	8.4	3+	0.9906	1.5080	...

at temperatures of 490° F. (254.4° C.) in air at 450° F. (232.2° C.) in a closed electrically heated kettle under a CO<sub>2</sub> blanket at 450° F. (232.2° C.). In this last method, a slight vacuum is also employed. The bodying rate of these two oils is discussed in detail in Chapter 3, Volume I.

It is to be noted that in the table describing the electrically heat-bodied oil under a blanket of CO<sub>2</sub>, the oiticica oil is always in a liquid state. This is due to the fact that the solid oiticica oil had to be liquefied for transfer into the kettle. Since there is a similarity between tung and oiticica oil, and since viscosity is still a variable of

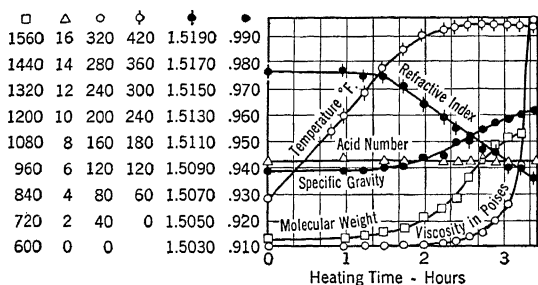


FIG. 28. Tung Oil Bodied in Air at 450° F. (12).

great importance in the practical relation of oils to paint, the molecular weight, refractive index, acid number, and specific gravity of the two oils are shown graphically in Fig. 29, as a function of viscosity.

The relationship of molecular weight is shown in Fig. 29A. The curves for the molecular weight increase for the two batches of oiticica oil bodied in air, are almost the same in the low viscosity region, and the curves separate more widely in the higher region, yet the general trend is the same. Since the rate of temperature rise for the oiticica oil bodied electrically is different from that in air, no comparison between these two is made. However, the curve of the electrically heated oil illustrates that the greatest increase in molecular weight is in the low viscosity region and again at high viscosity. The curve for the tung oil shows this same general trend. In the case of tung oil, there was a sudden increase in viscosity and a corresponding increase in molecular weight within less than ten minutes at the end of the bodying.

Figure 29B indicates that the refractive index decreases as the bodying or viscosity increases, and that the greatest decrease takes place at low viscosity; and then there is a correspondingly small de-

crease in refractive index for a large increase in viscosity. The oiticica oil bodied at 490° F. (254.4° C.) continues to decrease more rapidly than the other oils.

Figure 29C shows the relation of acid number to viscosity. With oiticica oil the great increase in acidity is developed in the low viscosity region. The oiticica oil bodied at 450° F. (232.2° C.) appears to develop more acidity than that which is bodied at 490° F. (254.4° C.); this is probably due to the fact that the oiticica oil bodies much more slowly at lower temperature, thereby giving it opportunity to develop more acidity. The tung oil developed practically no acidity.

Figure 29D shows that the specific gravity curves have similar forms for the oiticica oil bodied at 490° F. (254.4° C.) and 450° F. (232.2° C.). Tung oil shows considerably lower values than do any of the oiticica oils. The change of gelation time at various temperatures and at various viscosities of the two oils is given in Chapter 3, Volume I.

**General Remarks.** The bodying of oiticica oil can be more easily controlled than the bodying of tung oil.

Oiticica and tung oils are similar in physical behavior as indicated by the fact that the refractive index in both cases decreases with a corresponding increase in viscosity. It is to be noted that the refractive index of linseed oil (2, 7, 10) increases with increasing viscosity of the bodied oil.

The actual polymerization of oiticica and tung oil begins to show its effect as the bodying temperature is approached.

The gelation time [Browne heat test at 540° F. (282.2° C.)] can be used to determine the degree of bodying for tung and oiticica oils. Oiticica oil exhibits a minimum gelation time at 560° F. (293.3° C.).

After bodying or processing temperatures are fixed, viscosity can be used as a satisfactory indication of the degree of bodying.

### Fish Oil—Sardine Oil

The Los Angeles Club (6) has made a comparative study of the changes in physical and chemical properties of sardine oil during heat processing, has indicated the practical optimum kettling conditions required for proper bodying or polymerization, and has stated that properly winterized sardine oils of high iodine value polymerize readily. They have said also that, owing to the highly unsaturated eluponodonic glycerides present, sardine oils body faster than linseed oil.



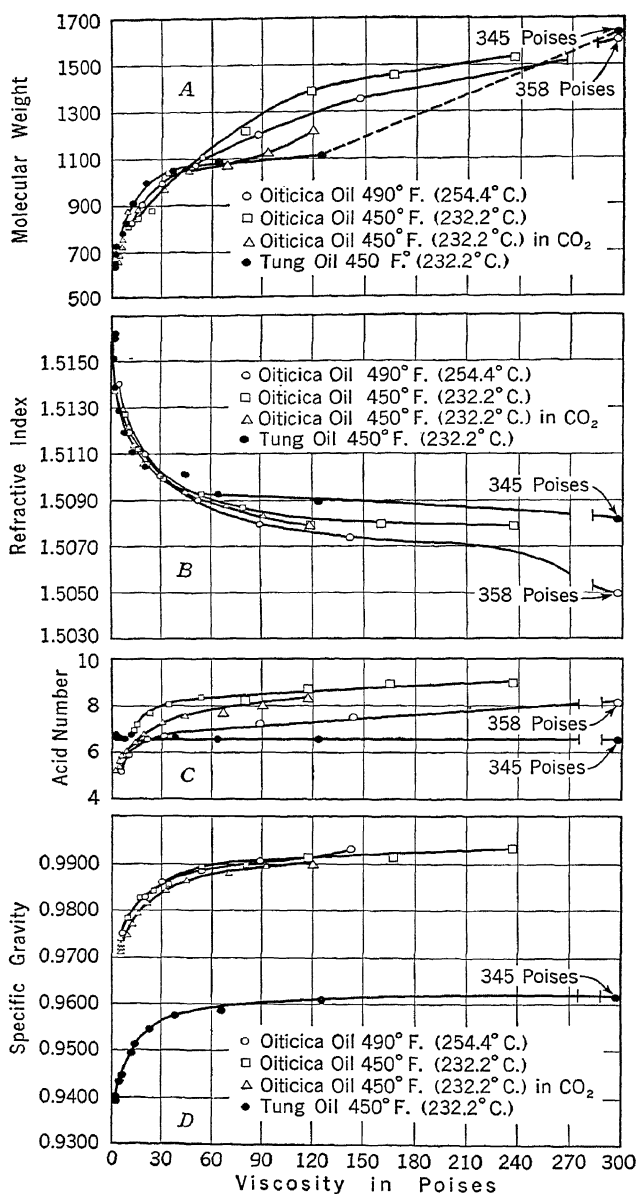


FIG. 29. Relation of Constants to Viscosity (12).

The oil used in this investigation was an alkali-refined and bleached California sardine oil with the following principal characteristics:

Color (Lovibond) .....	25 Yellow 3.0 Red
Chill test .....	Clear 8 hours at 32° F. (0.0° C.)
Free fatty acid (as oleic) ....	0.197
Iodine value (Wijs) .....	200.95

The properties studied were viscosity, molecular weight, iodine value, refractive index, and free fatty acid as oleic acid. These properties were determined as follows: viscosity by the Gardner-Holdt method; molecular weight by the Beckman method, using benzene as the solvent; iodine value by the Wijs method; refractive index with the Abbey refractometer; and the free fatty acid content by the usual alcohol-benzene solvent method.

Figure 30 shows the changes of the physical and chemical properties for sardine oil heat-processed on a commercial scale (150-gallon batch) with an open kettle at a temperature of 555° F. (290.6° C.). It required two hours for the temperature to reach 480° F. (248.9° C.) and then an additional two hours to reach 555° F. (290.6° C.). The batch was held at this temperature for eleven hours, at the end of which time the fish oil attained a viscosity of 148 poises ( $Z_6^*$  body).

The optimum kettling temperature for sardine oil is 535° F. (279.4° C.), as indicated by the rate of increase of molecular weights. This is shown in Fig. 31, for two commercial batches in which the increase in molecular weight is plotted against time in hours after a temperature of 480° F. (248.9° C.) has been reached. It is observed that the mean molecular weight of the oil bodied at 535° F. (279.4° C.) increased more rapidly and reached a higher value in less time than the molecular weight of the oil bodied at 555° F. (290.6° C.). It is also interesting to note that the fatty acid remained under 1 per cent for the oil bodied at 535° F. (279.6° C.) even after six hours of processing.

With fish oils, as with linseed oils (2, 7, 10), the refractive index increases and the iodine value decreases as the viscosity and molecular weights increase during the bodying.

The Los Angeles Club (6) noted that gel particles or polymer clouds were visible in all samples above 10 poises. The polymer cloud appears even in thoroughly winterized oils if they are bodied

\* Gardner-Holdt scale.

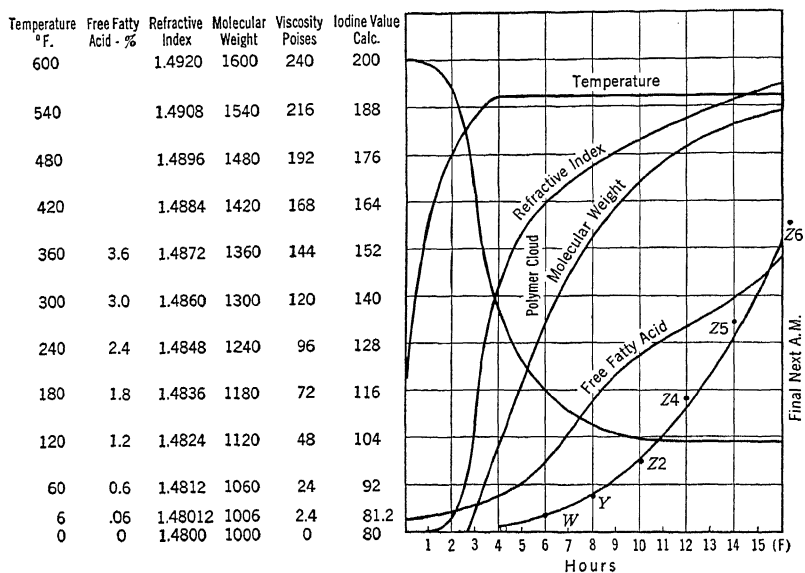


FIG. 30. Heat-bodying Fish (Sardine) Oil (13).

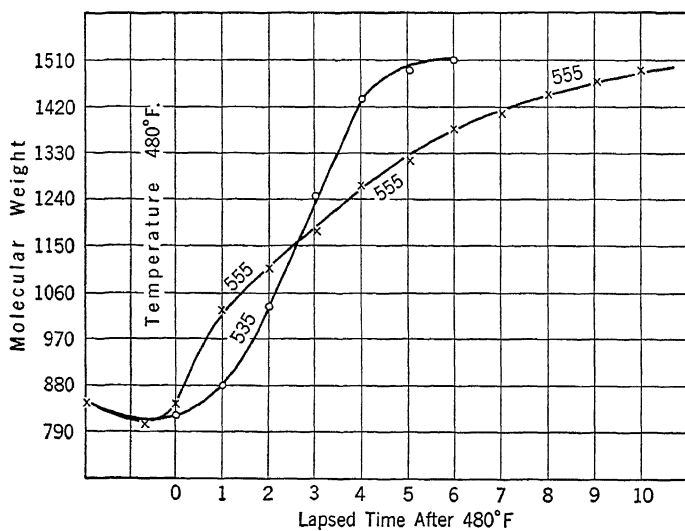


FIG. 31. Heat-Bodying Fish (Sardine) Oil (6).

to above 10.7 poises but it remains brilliantly clear indefinitely if bodied to 8.8 poises or lower. This phenomenon indicates that the safe optimum viscosity to which sardine oil may be kettled or bodied is 9 poises or lower. This work shows also that the polymer cloud is not a stearine or a glyceride containing a high percentage of saturated fatty acids, but it is composed of polymerized drying oils in coagulated gel particles which are insoluble at room temperature in the kettle oil. The polymer clouds which precipitated on long standing and the clear supernatant polymerized oils were tested for air drying. Both air-dried equally well within the same time. However, the clear film containing the polymer cloud dried flat and gel particles were visible in its surface.

For economic reasons, bodied fish oils of viscosity higher than 10 poises are desirable since they will stand more reduction or thinning with volatile thinners or solvents. It has been suggested that to develop higher viscosities in the range 98.0 to 148.0 poises, the sardine oil should be first heat-bodied to a viscosity of 9 poises at temperature of 535° F. (279.4° C.) and then increased further in viscosity by means of oxidation (air blowing under control conditions). This will give a more dispersed liquid phase than a corresponding body gained by the heating treatment alone. This oil will retain the advantages of a properly polymerized oil and have, in addition, the improved flowing, brushing, and leveling qualities of oxidized oils.

With sardine oil, as with linseed oils, the virtue of the polymerized oil lies in its increased molecular weight and increased density. These contribute to a decrease in the permeability of the dried film and to an increase in its gloss, water resistance, and durability from the standpoint of resistance to weathering by the elements.

### Dehydrated Castor Oil\*

Although the use of dehydrated castor oil in the paint and varnish industry has developed very rapidly, very little information is available concerning its bodying characteristics. This lack of data is due to the comparatively recent utilization (1939) on a large industrial scale of this oil in the industry.

The Cincinnati, Dayton, Indianapolis, and Columbus Paint and Varnish Production Club (3) have made a study of the bodying of both raw and processed dehydrated castor oil with equal parts, by

\*The remainder of this chapter was contributed by J. F. Gerkens and V. A. Kildare, Woburn Degreasing Co., Harrison, N. J.

volume, of soybean, fish, tung, perilla, and linseed oils and have recorded the bodying rates of these various blends in a commercial varnish kettle. von Mikusch (8) has presented a thorough study of the bodying rates of dehydrated castor oil at various temperatures and also has recorded the change of acidity during these operations. These data were obtained, however, from small-scale experiments in the laboratory.

Gerken and Kildare (4) have studied the change in physical and chemical properties occurring during the bodying of dehydrated castor

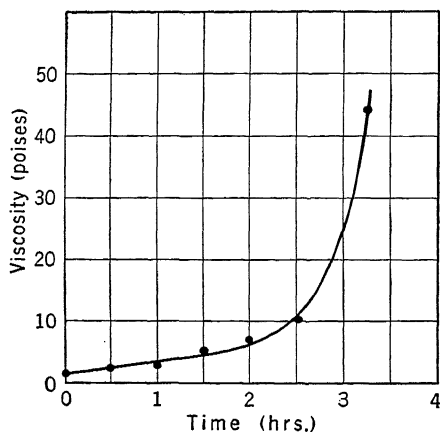


FIG. 32. Relation of Viscosity to Time—Bodying of Dehydrated Castor Oil to  $Z_3$  (appx. 44–50 poises) Viscosity at 550° F. (288° C.) in Vacuum (4).

oil by taking samples at regular intervals during the commercial bodying under a reduced pressure of 20–30 mm. and at a temperature of 550° F. (288° C.). In Table VII, these data have been tabulated and in Figs. 32, 33, and 34 they have been plotted to facilitate a rapid survey of these results.

The various methods of analysis used for these samples have been those described by Priest and von Mikusch (11). The iodine numbers were determined by the special Wijs method which employs an excess of at least 400 per cent of this reagent to obtain consistent results. The iodine number found by this procedure does not show the total unsaturation since this method indicates only one-half the total unsaturated conjugated double bonds. The method used for the determination of the diene value is essentially the method of Kaufmann and Baltes (5) with several minor changes as described by Priest and

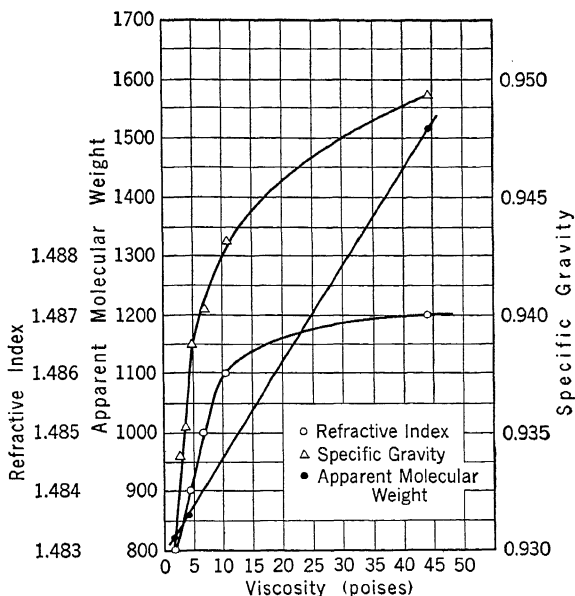


FIG. 33. Relation of Constants to Viscosity—Bodying of Dehydrated Castor Oil to  $Z_3$  (appx. 44–50 poises) Viscosity at 550° F. (288° C.) in Vacuum (4).

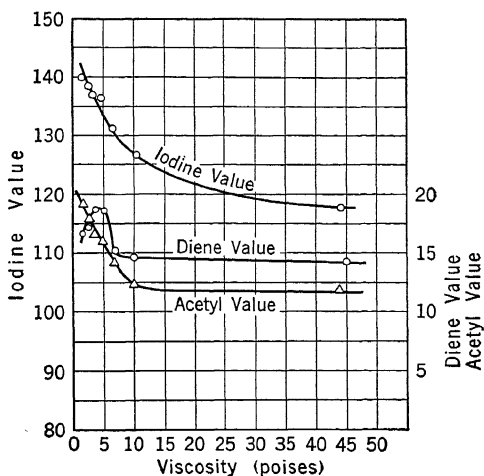


FIG. 34. Relation of Constants to Viscosity—Bodying of Dehydrated Castor Oil to  $Z_3$  (appx. 44–50 poises) Viscosity at 550° F. (288° C.) in Vacuum (4).

von Mikusch. The apparent molecular weights were obtained by the cryoscopic method with benzene as the solvent, and the results in Table VII indicate the averages of several determinations. In the determination of these molecular weights, to obtain concordant results, it was necessary to use sample weights of about 1.0–1.3 grams of the dehydrated castor oil dissolved in about 22 grams of benzene.

In Table VIII are recorded the analytical results obtained from the bodying of dehydrated castor oil of a  $Z_3$  (46.3 poises) viscosity to a viscosity of about  $Z_6$  (148.0 poises). This further bodying was conducted in the laboratory at a temperature of 520° F. (271° C.) and required a holding time of two and one-quarter hours to reach this viscosity. This operation was carried out in a large glass flask under gentle agitation with carbon dioxide. A survey of Tables VII and VIII presents some interesting facts regarding the chemical and physical changes which occurred.

TABLE VII

BODYING OF DEHYDRATED CASTOR OIL AT 550° F. (288° C.) UNDER A REDUCED PRESSURE OF 20–30 MM. HG

Temp. °F. (°C.)	Time, Hrs.	Vis- cosity, Poises	Iodine Number	Saponi- fication Number	Acetyl Value	Diene Value	Refract. Index, 27° C.	Spec. Gr., (25° C.)	Apparent Molecular Weight
	0	1.9	140.2	190.8	19.1	16.6	1.4832	0.9300	820
535 (279.4° C.)	½	2.6	138.8	190.8	17.9	17.21	1.4838	0.9340	
550 (288° C.)	1	3.4	137.0	190.6	16.8	18.8	....	0.9352	863
550 (288° C.)	1½	4.8	136.6	190.6	16.1	18.7	1.4847	0.9388	
550 (288° C.)	2	6.6	131.2	190.7	14.4	15.1	1.4851	0.9409	
550 (288° C.)	2½	10.3	126.8	190.4	12.3	14.7	1.4859	0.9432	
550 (288° C.)	3¼	44.3	118.0	190.1	11.9	14.3	1.4872	0.9494	1,515

TABLE VIII

BODYING OF  $Z_3$  (46.3 POISES) DEHYDRATED CASTOR OIL TO A  $Z_6$  (148.0 POISES) VISCOSITY IN THE LABORATORY AT 520° F. (271° C.)

Time, Hrs.	Viscosity, Poises	Iodine Number	Sap. Number	Acid No.	Acetyl Value	Diene Value	Sp. Gr., 25° C.
0	46.4	119.1	191.5	3.3	7.9	14.9	0.9489
2¼	160.8	117.0	191.7	4.3	4.9	12.8	0.9529

The acetyl value decreases steadily during the bodying operation from 19.1 on the raw dehydrated castor oil to 4.9 on the bodied oil with a viscosity of approximately  $Z_6$  (148.0 poises). This reduction indicates that either further dehydration or a condensation of the residual hydroxyl groups occurs. The acetyl value of an oil bodied to a  $Z_3$  (46.3 poises) viscosity is usually below ten.

The increase in diene value and the decrease in iodine number during the initial bodying period indicate that new conjugated bonds are formed until we reach a maximum at a viscosity of about 3-5 poises. Thereafter the diene value decreases steadily during the polymerization until at a viscosity of  $Z_6$  (148.0 poises) it is only two-thirds of its maximum value. This decrease in diene value from 18.8 to 12.8 represents a decrease from 21.7 to 16.8 per cent of the conjugated 9.11 linoleic glycerides.

The viscosity time curve plotted in Fig. 32 is a curve very similar to that obtained by Mattiello and Work (7) for linseed oil, although, as might be anticipated, it is much steeper. von Mikusch (8) has reported previously that dehydrated castor oil bodies three to four times faster than linseed oil and he has found the average doubling interval to be 26.7° F. (14.8° C.) and 23.4° F. (13.0° C.), respectively, for these two oils. In Fig. 33 the curve of specific gravity versus viscosity is also similar to that for linseed oil bodied at the same temperature (7). In Fig. 34 is shown graphically the relationship of iodine number, diene value, and acetyl value to viscosity. Table IX shows the average analysis of the bodied dehydrated castor oil of approximately  $Z_3$  (46.3 poises) viscosity.

TABLE IX

AVERAGE ANALYSES OF  $Z_3$  (46.3 POISES) DEHYDRATED CASTOR OIL

Color (Hellige) .....	1-2
Viscosity .....	44-50 poises
Specific gravity .....	0.949
Refractive index .....	1.4872 at 27° C.
Acid number .....	2-4
Apparent molecular weight .....	1,515
Iodine number (Wijs ½ hr.) .....	115-120 (400% excess)
Saponification number .....	190-192
Diene value .....	14-16
Acetyl value .....	below 10



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## CHAPTER 4

### CHEMISTRY OF THE HEAT-BODIED DRYING OILS

THEODORE F. BRADLEY

The art and skill of the old-time varnish maker have yielded slowly to the more scientific control and to the developments of the chemists and engineers who have entered the coating-materials industries. The complexity of the organic molecules which they have had to deal with, however, has necessitated the continued use of methods which, although more exact and more scientifically grounded than those of their predecessors, nevertheless are still quite empirical.

With the growth of the oil-processing and oil-consuming industries it became increasingly apparent that progress was largely circumscribed by the lack of adequate fundamental knowledge. On this account, during recent years, considerable support has been accorded the more fundamental investigations by a few of the larger industrial research laboratories.

Complementing these, numerous investigations of fundamental importance to the varnish industry have been accomplished in academic circles; thus, important advances have been registered from both sources. While attempting to summarize and to interpret the results of many of these investigations it is well to remember that the molecular complexity of the drying oils and resins which are now in commercial use has provided a formidable variety of problems which have long proved perplexing. Moreover, one should appreciate that the molecular complexity, i.e., size, structural configuration, and variety of molecular species represented, tends to become even more complex when one begins industrial processing, regardless of whether this processing merely involves exposure to heat, light, or oxygen, or the addition and blending of a considerable variety of oils, resins, and driers. Under such circumstances, one hardly need wonder that empiricism has so long prevailed or why there have been so many recorded differences of opinion and of conflicting experimental observations. The inherent complexity of the chemistry of these materials and of the processes employed in their utilization became most disconcerting

when analytical methods were applied in the attempt to accomplish their elucidation, and arguments arose as to the value and validity of nearly every analytical method chosen and applied to the problems at hand.

### Unsaturation of Drying Oils

At the present time, however, in view of the work of many investigators, it is possible to arrive at a fairly lucid, and probably valid, understanding of much of the chemistry of the drying oils and of the reactions which occur during their thermal treatment. It has been learned that the natural varnish oils are composed of the glycerol triesters of a variety of acids which vary mainly in the number and position of their carbon to carbon double bonds and, with the exception of certain of the acids of the fish oils, are almost exclusively members of the series which contains eighteen carbon atoms.

Of the eighteen carbon atom fatty acids it is further recognized that the degree of their unsaturation is important and that the three classes containing one, two, and three double bonds, respectively, are of particular significance since the speed with which the esters kettle body and dry is in part determined by the degree of unsaturation of their constituent acids.

Of perhaps equal importance is the position of the double bonds in the fatty acid radicals of these oils, since if two or more double bonds occur at alternate carbon atoms (conjugated unsaturation), the esters kettle body faster and frequently yet not invariably dry much faster than corresponding oils of equivalent degree of unsaturation but in which the double bonds occur more widely spaced (non-conjugated unsaturation).

Finally, with respect to the least unsaturated acids, it has been ascertained that acids which, like oleic and stearic acids, contain one or no double bonds contribute but little to the thickening of varnish oils during either thermal treatment or oxidation and serve mainly as diluents or softening agents.\* Actually, therefore, in the kettle bodying and drying processes alike, one is concerned almost exclusively with the poly-unsaturated acids, chiefly the doubly unsaturated or

\* Oleic esters, contrary to some opinion, are not inert since they undergo chemical and physical changes as a consequence of thermal treatment or of oxidation. These changes, however, are much less pronounced than in the more unsaturated esters and do not lead to gels or to dried films unless the alcoholic radical of the ester is derived from an alcohol containing an abundance of hydroxyl groups, generally in excess of three.

octadecadienoic acids and with the triply unsaturated or octadecatrienoic acids such as are listed in Table I.

TABLE I

## OCTADECADIENOIC ACIDS

Conjugated—10,12-linoleic—from alkali-treated, isomerized oils.

9,11-linoleic—from dehydrated castor oil or ricinoleic acid.

Non-conjugated—9,12-linoleic—from soybean and related oils.

## OCTADECATRIENOIC ACIDS

Conjugated—9,11,13-eleostearic—from tung oil.

9,11,13-licanic—from oiticica oil.

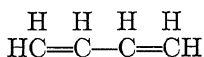
10,12,14—eleostearic—from alkali-treated isomerized oils.

Non-conjugated—9,12,15-linolenic—from linseed and perilla oils.

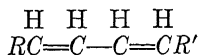
The theory of Scheiber (45), that the non-conjugated unsaturated fatty acids and esters tend to undergo a slow but progressive molecular change at elevated temperature involving a shift of their double bonds to conjugated position, has been experimentally confirmed by others (9, 11, 13), as one of the important changes which occur during stand oil formation, thus enabling one to direct particular attention to the conjugated octadecadienoic and octadecatrienoic acids.

## Relation of the Drying Oils to Polyene Hydrocarbons

Preliminary to the consideration of these acids and in view of the fact that most of their chemical reactivity is centered in their conjugated unsaturated systems, it seems advisable to stress the relationship of the 9,11-octadecadienoic acid and its esters to the conjugated hydrocarbon butadiene and of the 9,11,13-octadecatrienoic acid and



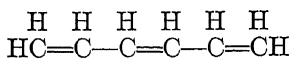
1,3-butadiene



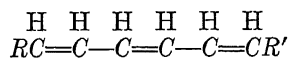
9,11-octadecadienoic acid

when  $R = \text{CH}_3(\text{CH}_2)_5-$

and  $R' = -(\text{CH}_2)_7\text{COOH}$



1,3,5-hexatriene



9,11,13-octadecatrienoic acid

when  $R = \text{CH}_3(\text{CH}_2)_3-$

and  $R' = -(\text{CH}_2)_7\text{COOH}$

FIG. 1. Structural Relation of Diene Hydrocarbons to Acid Radicals of Conjugated Drying Oils

its esters to the conjugated hydrocarbon hexatriene. In these hydrocarbons occur the analogous or simplified skeletons of the unsaturated portions of the drying oil acids (Fig. 1).

As early as 1912 Hofmann and Tank (26) reported that butadiene had been found to combine with itself to form a dimerized derivative which they announced to be vinylcyclohexene. Their experimental and analytical data were meager and were overlooked or too lightly dismissed by others until Lebedev and Sergienko in 1935 (33) and Alder and Rickert in 1938 (1) furnished more conclusive data and structure proof. The dimerization of butadiene to vinylcyclohexene, illustrated in Fig. 2, probably represents the first established case of that addition polymerization in which a conjugated diene reacts in the 1,2 position with another molecule of the same at the 1,4 position of the conjugate system. This reaction later came to be known as a special case of, or as a modified form of, the Diels-Alder diene synthesis and was first mentioned as the most probable mechanism of the polymerization of stand oils by Kappelmeier in 1933 (27).

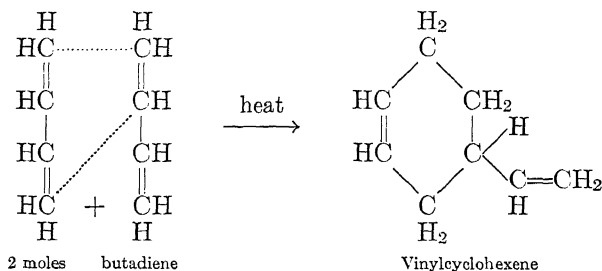


FIG. 2. Polymerization of Butadiene

During this period, many substituted butadienes were also investigated with respect to their ability to polymerize under a variety of conditions and with regard to the nature of such polymers. Prominent among such compounds were isoprene and other methyl- and dimethyl-butadienes. The work of Whitby and Gallay (48) in this field was particularly extensive. They noted that the degree and type of polymerization was profoundly influenced by the temperature and by the number of unsubstituted hydrogen atoms on the terminal carbon atoms of the compound. This is important for the proper understanding of drying oil polymerization since in this case one encounters (see Fig. 1) terminal substitution of hydrogen atoms by long chain alkyl radicals at the conjugated diene centers and also a comparatively high range of industrial processing temperatures, both of which

are known to be conducive to dimerization by the modified diene reaction rather than to those more extensive polymerizations which lead to rubber formation.

Recently the first comprehensive work on the synthesis of hexatriene and its polymers (30) has appeared, and as this work is extended by Kharasch and Sternfeld its relation to the thermal polymerization of tung and of oiticica oils and related esters will become more clearly evident. Here, too, is involved the 1,2-1,4-diene addition polymerization, leading in the case of hexatriene to a cyclized dimer 1-butadienyl- 2-vinylcyclohexene-3.

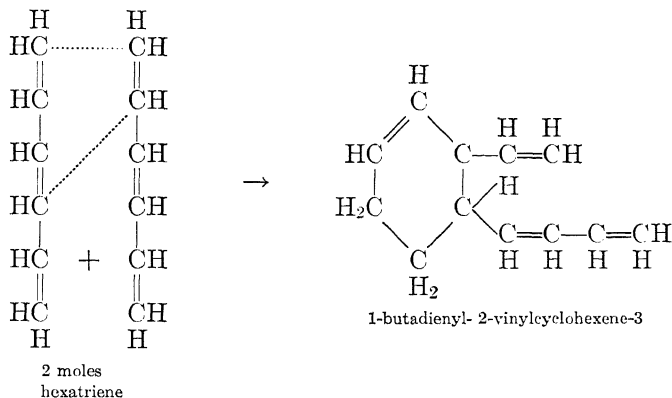


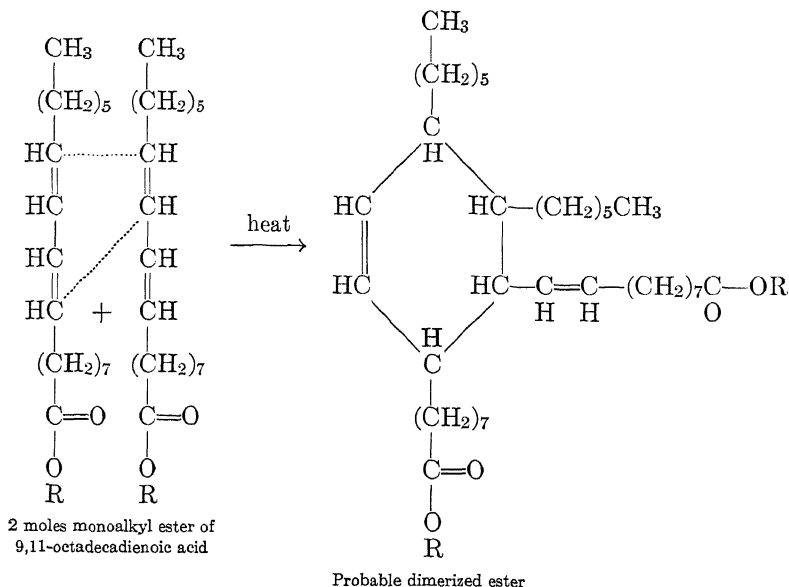
FIG. 3. Polymerization of Hexatriene

Somewhat higher polymers than these dimers, e.g., trimers and tetramers, are capable of being formed by similar mechanisms from butadiene and hexatriene owing to terminal unsaturation and the unsubstituted hydrogen atoms on these terminal groups. Nevertheless, the predominant polymer is invariably the dimer, and in the case of the unsaturated fatty acids of the drying oils one should expect the formation of dimers to be even more predominant for the reasons cited.

### Analogous Polymerization of the Drying Oils and of the Polyene Hydrocarbons

At sufficiently elevated temperatures one would expect the octadecadienoic and octadecatrienoic acids and their esters to undergo this analogous polymerization. Indeed this possibility had been conceived (27) and experimentally indicated (6, 9, 10, 11, 13) prior to the publication of much of the work with the hydrocarbons. The predominant

reaction in the thermal treatment of the natural drying oils and related esters has been shown to involve polymerization, the mechanism of which gives every indication of involving the dimerization of the fatty acid radicals by the 1,2-1,4 addition of the conjugate unsaturated systems resulting in cyclized linkages between the original molecules (6, 9, 11, 13). Bradley and Johnston (9) (see Figs. 4 and 5) have recently brought forth evidence that these linkages are monocyclic in the case of the octadecadienates as previously indicated by others but tend to become bicyclic in the case of the octadecatrienates because of the additional unsaturation which permits of a second and then intramolecular addition. This may help to account for the increased hardness of gels or films which are obtainable from products like tung, oiticica, and perilla oils as compared to those derived from dehydrated castor and soybean oils.



(Compare with dimerization of butadiene, Fig. 2.)

In comparing the polymerization of the conjugated polyene hydrocarbons with that of the conjugated polyene esters, one notes that while they are very similar there are important differences. In the esters, the occurrence of terminal substituents has prevented the formation of dimers containing the vinyl radical and has permitted the

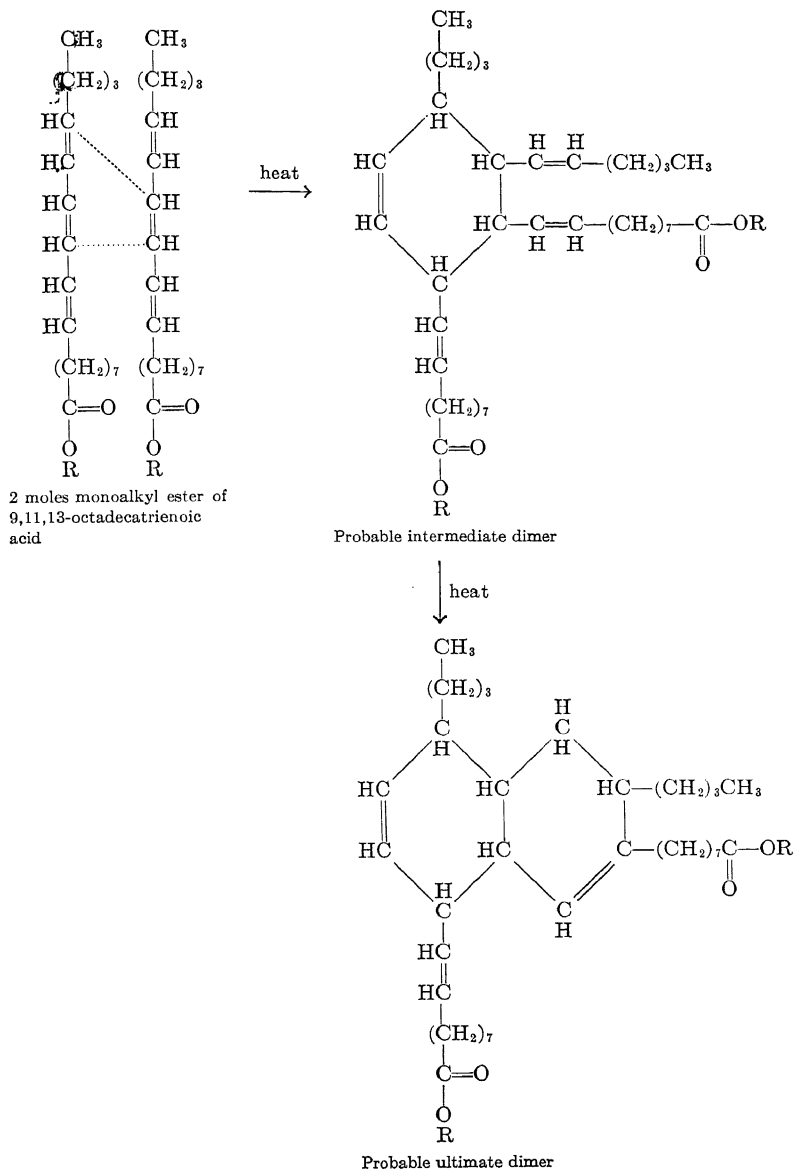


FIG. 5. Polymerization of Octadecatrienoate Esters.

(Compare with dimerization of hexatriene, Fig. 3.)



formation not merely of the structures represented in Figs. 5 and 6 but also of various unrepresented isomeric dimers. The detection and isolation of all the possible isomeric forms of these polymers and the determination of their structure remain to be accomplished. The absence of appreciable conjugation in the dimers of methyl and ethyl eleostearate, such as has been reported (11, 13) seems to indicate that the reaction has occurred mainly according to Fig. 5, i.e., through a medial double bond rather than through a terminal double bond, as in the case of unsubstituted hexatriene (Fig. 4).

Recently the author and his associates have shown how such dimers can be prepared in a high degree of purity by isolating the cyclic dimer of methyl linoleate by molecular distillation. This treatment also enabled the recovery of a small percentage of trimerized ester from the crude polymer mixture.

This work and the interpretations herein made have been considerably strengthened by the work of E. H. Farmer and Morrison-Jones (20) since they have found that the conjugated dienolic ester, methyl sorbate, which is structurally analogous to the conjugated methyl linoleates, also yields substituted cyclohexene dimers and a lesser proportion of trimers.

Further evidence has recently been obtained respecting the isomerization of unconjugated unsaturates to their conjugated forms, a step which, it will be recalled, is quite essential to facilitate the polymerization of the drying oils and of other non-vinyl type unsaturates. J. P. Kass and G. O. Burr (29) have shown that, by refluxing linseed oil or its fatty acids with alcoholic caustic, the linolenic acid is isomerized to 10,12,14-octadecatrienoic or pseudo-cleostearic acid. It has also been indicated that linoleic acid isomerizes under the same conditions to a conjugated form which is probably 10,12-octadecadienoic acid. G. O. Burr (14) has patented the production of isomerized fatty acids by the use of alcoholic alkalies. T. F. Bradley and D. Richardson (12) have since reported a feasible commercial process which requires only the use of water as a solvent.

The advantage of these processes is that their reaction conditions are sufficiently mild that but little of the isomerized products which are formed are destroyed by polymerization, unlike heat-bodied oils. Furthermore, the isomerized fatty acids may be re-esterified with polyhydric alcohols at sufficiently low temperatures, i.e., 190–210° C., still to avoid excessive loss of conjugation by polymerization.

The tendency of varnish oils to isomerize and then to combine with maleic anhydride by 1,2-1,4 diene addition has been described by

W. G. Bicksford, P. Krauczunas, and D. H. Wheeler (5). They have also indicated that a 1,2 addition with maleic anhydride occurs without loss of unsaturation by formation of substituted succinic acid derivatives in the case of oleic esters and of other unsaturated reactants containing only one double bond.

These diene reactions provide a mechanism by means of which the drying oils not only self-polymerize but also permit of the copolymerization of diene hydrocarbons (including the terpenes) and of many other unsaturated compounds (including rosin and ester gum) with the drying oils. Many such combinations have been effected during empirical studies and formulations with little or no appreciation of the chemistry involved. The fundamental investigation of many such diene reactions remains to be undertaken.

### **Influence of Alcohol and Acid Radicals**

Another important aspect of the chemistry of stand oil formation is the valency of the alcoholic radical which is attached to the unsaturated acids. This question has been explored by the author and his co-workers (6, 7, 8), and from the general principles of polymerization they have shown that the ester linkages and the double bond linkages are equally important and that the total number of intermolecular linkages must exceed two for each molecule in order to produce an insoluble, infusible type of gel. In the drying oil acids this necessitates coupling with an alcohol containing more than two hydroxyl groups to obtain gels and useful film-forming properties. After many demonstrations of these principles synthetic esters which could be gelled by means of both heat and oxygen were synthesized from polyhydric alcohols and maleic acid (7).

The influence of the alcohol radical is not due, as was formerly supposed in glycerides, to polyglyceride formation or to formation of acrolein and polymerization of the latter but involves a more general structural effect which follows the general rules of polymerization according to the functionality concepts. The alcohol radical is important and indeed effective in the drying oils only because it attaches to the carboxyl groups of the unsaturated acids and thus, strictly in accordance with its valency, acts to multiply the number of unsaturated radicals per molecule. Its effect is most simply illustrated as follows (Figs. 6, 7, 8), although it must be stated that the non-conjugated esters do not isomerize to conjugated form in the varnish kettle as fully or quickly as these figures might imply, their conjugation dis-

appearing almost as fast as formed because of thermally induced polymerization (11, 13).

In these figures the functional groups of the reacting fatty acids and the alcohols have been represented by black rectangular blocks. These groups comprise the hydroxyl group or groups of the alcohols, the carboxyl group of the acids, and also the two double bonds of the (in this case octadecadienoic) acid. *Viewed broadly, the initial step of esterification is a condensation reaction which may validly be regarded as the first step of polymerization if, like Carothers, one*

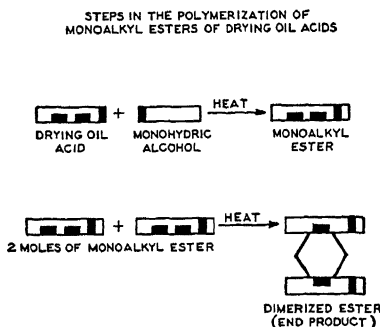


FIG. 6.

*refuses to completely divorce condensation from addition polymerization.* In Fig. 6 this step (of esterification) yields an ester which still retains the two double bonds of the acid, the acid and alcohol groups having merged to unite the acid and alcohol. In Figs. 7 and 8 this same step has yielded more complex esters, molecules of which contain more double bonds or potential polymeric functions simply because the number of hydroxyl groups per molecule of the alcohol which was involved has permitted of this greater accumulation.

The next step of polymerization involves an addition reaction in which half the original unsaturation or one double bond of the fatty acid radical is exhausted. This reaction unites one acid radical with another, forming an ester of a dibasic acid. This is the identical reaction represented in Fig. 4 and of the same type as that of Fig. 2. The latter is not at all complicated but, when an acid group is substituted for hydrogen of butadiene, ester formation becomes possible, and the complexity of this ester will vary with the number of hydroxyl groups of the alcohol used for its esterification. This difference of complexity is illustrated by the dimers of Figs. 6, 7, and 8. This difference becomes further exaggerated beyond this point for the re-

activity of the dimer of Fig. 6 is practically exhausted (because of loss of conjugation), that of Fig. 7 is no greater than that of the original ester (because the degree of conjugation per mole, but not per unit weight, is the same as that of the original ester), while in the glycerol ester of Fig. 8 the reactivity increases at each step because

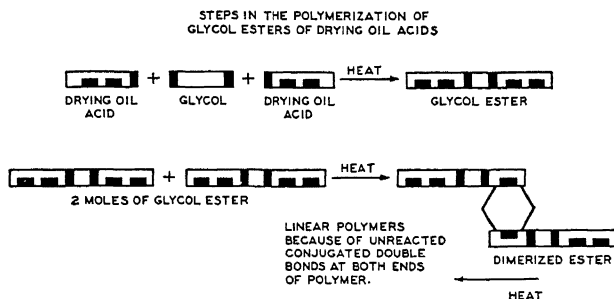


FIG. 7.

each new mole accumulates more and more reactive groups and permits of a most complex three-dimensional growth. Gelation and good film-forming characteristics for esters of these three types are apparently confined to those of Fig. 8.

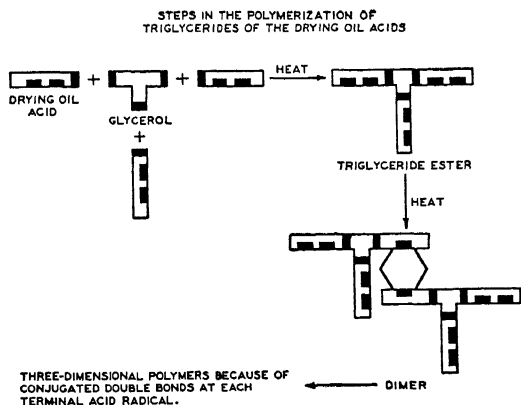


FIG. 8.

Some of these concepts were stressed by the author in 1937 (6) at which time it was shown how well they agreed with the general principles of polymerization suggested by Carothers (15) and by Kienle (31). Only when the total functionality exceeded two was it possible to obtain gelable and "drying" type compounds of commercial utility.

In one publication (6) it was reported that after their polymerization the esters could be saponified and the soaps hydrolyzed to obtain a mixture of dibasic and monobasic acids. More recently it was shown that the ratio of dibasic to monobasic acids recoverable from the heat-treated esters was determined by the degree of polymerization as well as by the extent of any other addition reactions which had involved the double bonds (10). The observed relationships disclosed that the addition reactions involved not only polymerization (intermolecular reaction) but also intramolecular additions, which apparently also include some ring closures. These conclusions, moreover, agreed with those previously derived from the iodine value-molecular weight relationships (8).

### Decomposition Reactions

Much less prominent, yet nevertheless important, reactions which occur during the kettle treatment of drying oils and related esters are those which involve thermally induced rupture of the molecules. Naturally the nature and extent of these may be expected to vary with the time and temperature of the treatment and may assume various forms. Aside from the well-known rupture of ester linkages, creating free acids, the remaining types of decomposition and the nature of the products formed have only recently been investigated (9). It is important to observe that because of the longer time required to body the oils which contain mostly non-conjugated acid radicals, the decomposition reactions become more predominant in their case than with the conjugated esters; that even the oleic acid radicals participate in these reactions; and that the composition and nature of stand oils are appreciably affected by these side reactions as well as by the degree of polymerization (9, 10, 11).

Specifically, it has been found that variable, yet usually small, amounts of the unsaturated esters tend to rupture at or near the center of the fatty acid radicals, yielding unsaturated hydrocarbons such as octene and possibly dienes together with acids and esters of reduced molecular weight such as the decenoates; also, that some of these fragments tend to re-unite and form "abnormal" polymers of molecular weights intermediate between the original esters and their true dimers. The full nature and scope of these thermally induced side reactions remain to be determined, especially since definite indications appear that migration and exchange of hydrogen atoms occur to some extent, resulting in the formation of at least spectroscopic amounts of aromatic compounds and of small amounts of saturated

esters (9, 10, 11). Moreover, the monobasic, and therefore presumably unpolymerized, fatty acids recovered from highly polymerized stand oils or their methyl esters have been found to differ from the original acids, being more saturated and possessing different absorption spectra (9, 10, 11). Further investigation is therefore necessary to clarify these phenomena.

### Methods of Investigation and Results

Studies based upon the synthesis of resins, oils, and polymers have thus far been found more helpful in elucidating the chemistry of stand oil formation than have purely analytical studies of the latter. One reason is the non-volatility and complexity of the products investigated, and another reason is appreciable doubt in many quarters of the reliability of the analytical procedures employed. However, in this case the concepts of polymerization have provided simple, mathematical yardsticks which help to evaluate these analyses (8), and, in addition, new analytical tools have recently been applied by physicists in the form of ultraviolet and infrared absorption spectra, the preliminary results of which appear most encouraging and favor present conceptions (2, 3, 11, 12).

The absorption spectra appear to be independent of particle size or molecular weight and to be extremely useful in following the course of reactions in complex organic molecules. At the present time some difficulty is encountered in the interpretation of these spectra, particularly the infrared, because of an insufficient amount of fundamental data which can be obtained only from the examination of hundreds of pure compounds. Sufficient data, however, have been obtained to show that the ultraviolet absorption spectra can be used to detect and distinguish double and triple forms of conjugation and to estimate the percentages thereof, to follow changes in the degree of unsaturation during the course of polymerizations and hydrogenations, and to provide some indications of structural changes as, for example, from straight chain to cyclic configurations (11). The infrared absorption spectra also provide evidence concerning the presence or absence of the several forms of conjugated unsaturation as well as of other forms of unsaturation. Unlike the ultraviolet spectra, the infrared absorption spectra also provide evidence concerning the presence of hydroxyl, carbonyl, ether, and many other groups or radicals (2, 3). Within a few years the utility of these tools is expected to become more widely recognized and accepted.

Some progress has been made in fractionating the relatively non-volatile stand oils and in learning to distinguish and to make use of the chemical and physical differences of the isolated fractions following solvent extractions (4, 21) or molecular distillations (42). Somewhat greater scientific progress, however, has attended the extensive use of the methyl and ethyl esters of the drying oil acids for the study of drying oil polymerization since this effectively limits the size of the polymers (see Fig. 6) and permits of the complete removal of unpolymerized constituents by vacuum distillation or solvent extractions. Particular credit is due Kino (32) and Steger and Van Loon (46) for their introduction and extensive use of this means of investigation, the results of which, together with the more recent work of Brod, France, and Evans (13) and of the present author and his associates (9), have been previously embodied in this chapter.

Although comprehensive analyses of the total bulks of stand oils such as have been made by Mattiello and his co-workers (39) have been of much value for standardizing and controlling the reactions, fractionations have enabled a greater insight into the nature of the mixtures therein represented. The highest polymeric fractions of stand oils isolated in a form which is still soluble in organic solvents have been reported by Elöd and Mach (19), by Gay (22), and by others (42) using diverse molecular weight methods, to possess molecular weights between 3,500 and 4,300, whereas polymerization theory has indicated that at least twice this average molecular weight is attained when complete heat-induced gelation is achieved (10). The average molecular weight of stand oils, however, seldom exceeds 2,500 owing to the percentage of polymers of low molecular weight, unpolymerized constituents, and products of thermal decompositions.

The colloidal or association characteristics of these polymers have received much attention and have been employed by some in an attempt to explain the oil-bodying and drying phenomena. At the present time, however, it becomes increasingly evident that these colloidal characteristics are derived from the molecular structure and from the degree of polymerization of the reactants; hence, while of unquestioned importance and influence, they are of secondary origin and significance. Unless and until the molecules have polymerized to adequate size and complexity of structure, the secondary valence or association forces do not appear adequate to effect gelation or useful film formation. The secondary valence forces are believed to figure most prominently during oxidation of the oils and there to involve

some "hydrogen bonding," through hydroxyl and peroxide intermediates.

The diene reactions of the drying oils and cognate substances provide a mechanism which can be extended to include the reactions between the oils and rosin as well as a number of other varnish constituents and, together with the side reactions and isomerizations which have been briefly mentioned, provide a foundation upon which one may begin to explain many empirical observations and upon which may be based future research and development. The faster drying and bodying of tung, oiticica, and dehydrated castor oils as compared to perilla, linseed, and soybean oils have been found definitely to be due to the conjugated unsaturation of the first group, a form of unsaturation which most readily tends to undergo polymerization. One trend of research, therefore, will be toward the formation of conjugated from non-conjugated systems and toward methods of increasing the unsaturation of those oils which are now too low in their degree of unsaturation. Another trend will involve the more extensive investigation and use of purification methods whereby stand oils of more nearly perfect and uniform quality may be derived. The synthesis of new and useful drying oils and resins, in addition to those which have already appeared, may be anticipated. Continued and more extensive research investigations will be required to accomplish these objectives.

### Oxidation and "Drying" of Stand Oils

Although many aspects of the oxidation and "drying" of oils have been treated in another section of this book and reviews of the subject have been published recently (15, 43), there remain certain details which may be examined profitably.

If the reactions involved during the thermal treatment of stand oils are acknowledged to be complex, how much more complex must appear those oxidation reactions which similarly affect the thickening and gelation of the oils? Many more years may pass before an adequate knowledge of these reactions is attained, yet there appear to be basic principles common to both the oxidized and thermally processed oils which should be recognized before one becomes too immersed in the maze of oxidation reactions. These principles, derived from the general rules of polymerization, have been mentioned by Sorensen (Chapter 1, Volume I), and detailed elsewhere (6, 7). With respect to the oxidized oils, they point to the fact that the gelation and film-forming properties are analogous to those of the heat-thickened oils and that



the recovered acids on hydrolysis, although oxidized, are predominately dibasic. Therefore, the basic principles are identical even though one may cyclicize the acid radicals by direct carbon to carbon linkages in one case or by carbon to oxygen to carbon linkages in the other. Because they are analogous, except as to the exact details of the mechanism, it follows that they should be so interchangeable that, if one partially thickens an oil by heat alone or by oxygen alone, a lesser amount of heat or of oxygen will be required to complete the job or to gel the oil than would have been the case when the alternative means was solely employed. In other words, there is a substantial mutual equivalency and exchangeability between heat and oxygen as a means of thickening the oils. True, chemical and physical differences exist that affect their relative technological values, yet fundamentally the aforesaid relationship exists.

Another and related fundamental aspect is that unless one is dealing with molecules that possess the correct number of reactive or functional groups, one may load the molecules with oxygen to the saturation point and never obtain a "dried film" in the usual sense of that word. One may consult the literature and find much illustrative data. To cite a few cases, Rhodes and Ling (44) found raw tung oil to require 44 per cent of oxygen, whereas heat-bodied tung oil absorbed but 29.5 per cent of oxygen. Long and McCarter (34) found the methyl esters of linseed oil acids to absorb 30 per cent more oxygen without gelation than was required to gel the glycerol ester. Similarly, the more poly functional pentaerythritol ester and the heat-bodied glycerol esters required much less oxygen to attain gelation than the unbodied oil. They stated "as the complexity of the molecule increases, the rate of oxygen absorption decreases and less oxygen is required for gelation." Modern concepts seek to clarify the term "molecular complexity" and attempt to develop its full meaning.

The case may also be cited of certain unsaturated hydrocarbons such as the polyterpenes which upon exposure to the air are known to absorb oxygen and be converted from a liquid into a hard, somewhat brittle, yet tacky, film. Some might say that these had dried. According to the author's observations, however, these films are not "dry" in the full sense of that term since they fuse and soften easily like many resins and are easily dissolved by numerous organic solvents. The soft resin or balsam has merely oxidized and increased in softening point yet remains a linear polymer or thermoplastic. Present concepts attribute this and the case of the mono alkyl esters of the drying oil acids to lack of an adequate number of functional

groups such as will permit of the formation of a three-dimensional polymer.

From these relationships it appears that oxygen induces the polymerization of the fatty acid esters much the same as does heat. Beyond that point difficulties arise *because oxygen can function in so many different ways, depending upon the compound being oxidized and upon the environmental conditions*. Small amounts of oxygen, yielding peroxide intermediates, are known to initiate chain polymerizations in many vinyl compounds. Oxygen may also fully saturate the double bonds of other compounds such as the drying oils and effect polymerization mainly through condensation reactions involving the formation of carbon-oxygen-carbon linkages. Oxygenated, especially hydroxylated, intermediates may undergo a looser form of polymerization through residual valence or dipole forces such as the well-authenticated "hydrogen bonding" of hydroxyl-bearing compounds. *It is probable that each of these three modes of oxygen activity is involved in the oxidation and "drying" of the varnish oils* and, occurring together, are difficult to dissociate sufficiently for exact determination.

The polymerization characteristics of the natural drying oils, indeed of all unsaturated compounds, have suggested that carbon to carbon double bonds are not equivalent and that they, like oxygen, may alter their mode of activity according to the structure of the molecule as a whole, particularly with regard to the nature of adjacent groups and with the environmental conditions. Ample evidence was found to support this in unsaturates of low molecular weights, but only recently, through the work of Morrell and his associates (40), do we find this also true of the drying oils. In  $\beta$ -eleostearine and its maleic anhydride adducts, considerable evidence has been found to the effect that the double bonds most remote from the carboxyl group of each fatty acid radical tend to add oxygen as peroxide and then to polymerize by rearrangement at this point, whereas the double bonds nearest to the carboxyl group tend to form ketols which may not assist polymerization.

With Morrell's support a novel investigation was conducted by Gee (23). Applying the Langmuir trough, the eleostearine adducts were studied in the form of monomolecular layers. As the molecules spread widely apart they oxidized, yet could not polymerize, whereas when brought together and compressed they immediately polymerized or associated. Subsequent work by Marsden and Rideal (38) showed that films could also be formed by the association of certain dihydroxy acids when in the *trans* but not the *cis* configuration, a phe-

nomenon which was definitely traced to polymeric hydrogen bonding between hydroxyl groups. Similar bonding may have been involved in the first instance, but it seems probable that primary valence forces were mainly at work in that case. Unfortunately, the solubility and other characteristics which would decide this point were not made evident.

In the recent work of Carrick and his associates (16) also is evidence that during the oxidation of tung oil the several double bonds function differently, the first being oxidized rapidly without loss of diene value (hence retention of double conjugation, yet loss of triple conjugation). Little or no volatile matter was eliminated until the second double bond had begun to oxidize, and the loss of volatile matter became great only during the oxidation of the third double bond. They showed also that the percentage of acetone insoluble matter (polymer) rose rapidly to a maximum while a dry film was forming and before the second double bond had completely oxidized. The loss of weight during the oxidation of the third double bond was accompanied by the formation of acids. A general and large increase in the saponification number was observed throughout the oxidation, probably denoting the formation of new species of lower molecular weight as the unit of the polymeric structure.

The aforementioned work also shows that the peroxides which are formed are considerably more stable than has commonly been supposed (even in the presence of driers which greatly expedite their decomposition) and reach a maximum concentration during the period in which the film and the bulk of the acetone insoluble product are formed. In view of this and of the early and large increase of saponification value, it appears that the "peroxide value," but not necessarily the peroxides, bears less relation to the polymerization than some publications would indicate. In this connection, the relative stability of the peroxides becomes of much significance.

Working with linseed oil at high dilutions in carbon tetrachloride and effecting oxidation at the boiling point (of 79° C.), Ward and France (47) reported that no peroxides could be detected and that nearly half the double bonds had been oxidized before insoluble polymers appeared.

The work of Nakamura (41) and of Franke and Jerchel (21) throws much light upon the variable velocities of peroxide formation in different oils as well as of their rates of decomposition. The double bonds oxidize at different rates. The oxidation of tung oil differs considerably from that of the non-conjugated oils.

The following data are of particular significance (41):

TABLE II

Oil Tested	Optimum Temperature of Peroxide Formation, °C.	Decomposition Temperature of Peroxides, °C.
Soy	80-100	110
Castor	155	110
Linseed	105	80
Tung	95	40

Metallic driers and active clays reduce the decomposition temperature of the peroxides. These data do not imply that the peroxides will not decompose at room temperatures. They do, but as Carrick's data (16) show, the process is very slow at normal temperatures, especially in the absence of metallic catalysts.

The collective evidence apparently shows that the polymerization and film formation of tung oil occur at an early stage of its oxidation and that much undesirable oxidation with formation of decomposition products sets in during the later stages.

On the other hand, many experiments show that the oxygen-induced gelation of linseed oil sets in at a later stage of its oxidation, a phenomenon which is analogous to the comparative rate of gelation of these oils during thermal treatment. Oxidation, like heat treatment, also promotes the formation of more molecular rearrangements and of decomposition products of low molecular weight in the case of the linseed oil as compared with tung oil. Some of these derivatives of low molecular weight may be solvent-extracted, and their removal tends to render the film harder and more water resistant.

The solvent extraction of both heat-thickened and oxidized oils to remove unpolymerized or slightly polymerized esters and their decomposition products is a well-known laboratory and, frequently, a commercial procedure. Elm (18) and others have stated that, aside from their degree of polymerization, the soluble fractions hardly differ from the insoluble fractions and point to the variations of the percentage extractable by different solvents as an argument that these oils are association colloids and not polymers at all. The writer disagrees with these views. *In the solvent extraction of gels, much care must*

be taken to use only chemically inert liquids and to secure adequate contact of all portions with the extracting liquid.\* Some variations arise from this source. Larger variations arise because one is dealing with diverse molecular species, the solubilities of which are bound to vary in different solvents. No better illustration need be cited than the work of Long, Rheineck, and Ball (35) wherein dried films of linolenic glyceride were extracted with various solvents of the ester, ketone, alcohol, chlorinated hydrocarbon, and hydrocarbon types.

The following values were reported:

TABLE III  
ANALYSIS OF LINOLENIC GLYCERIDE FILMS

Solvent	% Extracted Liquid	% Combined Oxygen	
		Liquid Phase	Gelled Phase
Acetone	29.5	38.4	29.8
Ethylene dichloride	32.9	35.9	28.8
Chloroform	30.6	32.4	30.8
Methyl acetate	36.6	33.7	30.8
Methanol	50.8	35.2	29.0
Ethanol	50.1	30.4	29.1
Benzene	13.4	25.7	29.4

Highly polar or hydroxylated constituents should be least soluble in benzene and most soluble in alcohols, as observed.

Other data on linseed oil and trilinolenic glyceride films were reported as shown in Table IV (35):

In this work the analyses almost invariably show a small but probably significant difference in the state of oxidation of the two phases. Writers previously have dismissed this difference as negligible or within experimental error and have maintained that the only real difference is in the state of polymerization or association. This may be questioned and more extensive analyses advised to settle this matter. The aforementioned work shows the liquid or ungelled phase to be some-

\* Since the peroxides have been found by the author to be reactive with both carboxylic acids and aldehydes, much work involving the use of acetic acid and the like must be questioned.

TABLE IV

PERCENTAGE OF OXYGEN CONTENT OF ACETONE-EXTRACTED FILMS

Age of Film (Days)	Linseed Oil		Trilinolenic Glyceride			
	Outside Exposure		Outside Exposure		Inside Exposure	
	Soluble Phase	Insoluble Phase	Soluble Phase	Insoluble Phase	Soluble Phase	Insoluble Phase
3	26.6	....	32.43	28.83	30.14	....
16	34.29	....	37.88	29.65	31.05	29.7
35	33.30	....	33.40	30.76	34.13	30.48
123	40.72	38.4	....	34.45	35.0	29.90

what more oxidized than the gelled, insoluble phase. On the other hand, in a previous work by Long, Zimmermann, and Nevins (36) the following ultimate analyses were reported:

TABLE V

Oil Represented	Carbon, %	Hydrogen, %	Oxygen, %
1. Raw linseed	78.96	10.69	10.35
2. Linseed film 63 days old			
61.5% gel	63.4	8.7	27.89
38.5% soluble			
3. Soluble fraction from above (2)	65.35	8.75	25.90
4. Film 114 days old unextracted	63.36	8.63	28.01

This work demonstrates just the reverse of what was subsequently reported since the data indicate the insoluble fraction to be more oxidized than the soluble fraction. In this dilemma the author may point to the unpublished work of his associates, R. T. Dean and H. F. Pfann. They oxidized an alkyd resin which had included 30 per cent of linseed oil in its formulation and 0.05 per cent of cobalt based on this oil content. The oxidation was carried well beyond the gel stage by continued agitation in a W & P mixer in the presence of air at

77 to 95° C. The gels were extracted with acetone at appropriate intervals and the fractions found on ultimate analyses to be as follows:

TABLE VI

Time (Hrs.)	Soluble Phase			Insoluble Phase		
	% C	% H	% O	% C	% H	% O
0 (initial)	69.5	9.3	21.0	....	...	....
4	66.8	8.8	24.3	65.2	8.5	25.6
8	66.9	8.9	24.1	65.0	8.3	26.5
12	66.9	8.9	24.1	65.3	8.4	26.4
18 (final)	66.1	8.8	25.0	64.7	8.1	27.1

This work shows the insoluble phase to have been more highly oxidized than the soluble phase and the difference to have been of the order of 50 per cent more oxygen absorption for the insoluble than for the soluble phase. Temperature and other reaction conditions doubtless influence these results.

Elm (18) has reported the soluble fractions isolated from oxidized linolenic glyceride films to range from 995 to 1,132 in molecular weight. The soluble fraction of heat-gelled oiticica oil was found by others to possess a molecular weight of 1,157 to 1,195 (10). The total acids recovered from the latter differed from those which were isolated from the insoluble fraction not only in their ratio of mono and dibasic acids but also in their absorption spectra (10) and (11) and other constants. It is therefore believed that future work may establish important differences between the acids recovered by the hydrolysis of the soluble and insoluble fractions of oxidized oils.

Condensation reactions *which, because of the plurality of functional groups, may become condensation polymerizations* (15) have been definitely established during the oxidation of the vegetable oils, at normal and at more elevated temperatures. They were shown by Long and others (35) to yield as much as 4.5 to 9.6 per cent of water, 2.6 to 4.7 per cent of carbon dioxide, and 6.1 to 9.5 per cent of volatile acids based on the weight of oil used during the drying of linseed oil at 7° C. and 52° C. Driers increase the rate of formation and amount of these volatile by-products. The products which had been dried at 7° C. evolved about 50 per cent more volatiles when subsequently

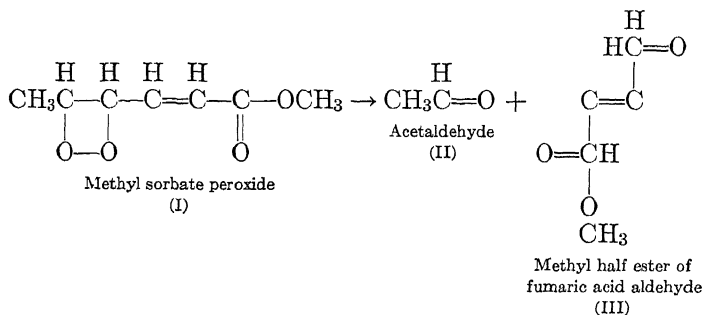
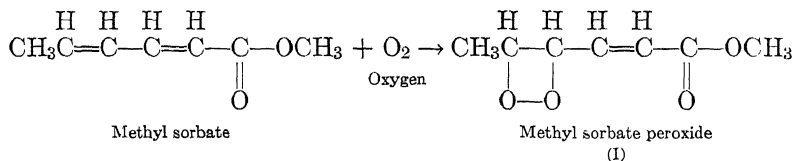
heated to 52° C. than had been produced during their original oxidation. The increase of the acid number, of the saponification value, and molecular weights of the oils during film formation by oxidation offers further evidence that condensation polymerization between polar groups rather than addition polymerization is the chief mechanism involved. The ability of fatty acids to promote the oxygen-induced gelation and drying and to enter into chemical combination with the intermediate oxygenated compounds was established by Long and his associates (34). This forms a significant exception to the analogy between oxidized and heat-gelled oils since free fatty acids retard heat gelation. Only in the former case is condensation polymerization possible. In the latter, an addition reaction which restricts further polymerization is known to occur. That either condensation or addition mechanisms of polymerization may yield gelled products and films is established in the case of phthalic glyceride and divinyl benzene, respectively. When both mechanisms can operate at one and the same time they both act to effect gelation, and if we establish some point, such as the gel point, or a given viscosity, as the end point of a reaction in such a hybrid system, we can reach this particular end point by either mechanism or both in varying degrees, according to the experimental conditions. Such a system was found in the glycol-maleic poly esters, this constituting one of the first synthetic drying oils (7). The natural drying oils constitute related, yet not identical, hybrid systems.

From all the evidence cited, it may be finally concluded that *the drying mechanism can and does vary* according to the structure of the molecule (especially the type and degree of unsaturation) and with the environmental conditions (especially the temperature). The "drying" of linseed oil apparently involves more condensation reactions and less addition reactions than in the case of the conjugated ester; tung oil, and raw oils, more condensation than the heat-bodied oils. Glycol-maleic esters can be prepared in such a manner that one can control and separate the condensation from the addition reactions. After the condensation has been stopped, oxygen-induced addition polymerization (to yield dried gels and films) has been found possible, the oxygen consumption being but a fractional percentage. The amount of oxygen required, however, varies with the chain length of the polymer and may thus yield the required cross linkages by the formation of substituted dioxane rings. It is possible that some of these are also formed during the drying of the natural drying oils as suggested by Marcusson (37), an hypothesis which ties in well with the



formation of dithiane rings in the sulfur and sulfur monochloride bodied oils (28) and with the formation of the six-membered cyclohexene rings in the heat-bodied oils. On the other hand, in concluding the citation of the more relevant experimental data and to *again emphasize the diverse mechanisms which serve to bring about gelation and film formation*, the work of the Finnish chemist, Pekka Heinanen (25), must be considered.

Heinanen studied the oxidation of methyl sorbate by air, hydrogen peroxide, benzoyl peroxide, and ozone. Of these only ozone effected oxidation of both double bonds; the others acted only on the double bond most remote from the ester linkage. Peroxides were formed which differed somewhat in each case, that which was formed from air being most relevant to the present discussion. The formations of this peroxide and of its subsequent derivatives are best illustrated by the following equations:



Compounds II and III also took on additional oxygen to yield acetic acid and the methyl half ester of fumaric acid respectively.

Another reaction product which was isolated was a tetrameric form of sorbic ester peroxide, a substance which was also capable of decomposition to yield compounds II and III. In the light of the polymerization theory this conversion of the monobasic acid ester to a dibasic acid ester would provide a mechanism whereby the glycerol ester of sorbic acid could be expected to undergo oxygen conversion or "drying."

The formation of acetaldehyde and the methyl half ester of fumaric acid aldehyde together with their corresponding acids during the oxidation of methyl sorbate finds its exact counterpart in the oxidation of methyl oleate at 75° C. where pelargonic aldehyde and the methyl half ester of azelaic acid aldehyde and their acids have been reported (17). In this latter case, however, the peroxides are found to undergo several additional forms of cleavage. Each double bond consumes about four atoms of oxygen, of which one is eliminated together with two "stolen" atoms of hydrogen as a molecule of water.

Of particular significance in the work of Deatherage and Mattill (17) is their finding that oxido esters (mono oxides or substituted ethylene oxides) are formed during the oxidation of methyl oleate and of oleyl alcohol but not in the case of oleic acid. In this latter case it was shown that the carboxyl group of the acid reacted with the oxido group to form esters. This conforms well with the previously cited work of Long and of others on the linseed and other of the more unsaturated oils and indicates that the increased saponification number which attends the oxidation of these oils is due to this form of reaction. This type of condensation provides an additional means whereby polymerization and "drying" may result.\*

The rules of polymerization teach us that in the case of a natural drying oil (triglyceride of an unsaturated monobasic acid) it is merely necessary to find some way to dimerize the acid radicals or a fragment thereof in order to enable an intermolecular reaction that can lead to gelation or "drying." Any mechanism which accomplishes this intermolecular reaction may serve to effect "drying," the present evidence seeming to show that indeed a number of reactions do occur simultaneously and each will vary in degree according to the type of unsaturation of the reactants and with the environmental conditions, especially the temperature.

Future work may be expected to result in the recognition and classification of the several forms of oxygen-induced gelation or "drying." †

\* The author and his associates have found, in work as yet unpublished, that the peroxides which are formed during the "drying" of oils are capable of combining both with free aldehyde and with free carboxyl groups to form hydroxy esters in each case. These esterifications do not require the elimination of water and proceed easily at even room temperatures. Since the rupture of peroxides is known to yield aldehydes, which in turn may also yield acids, a mechanism is thereby evident whereby hydroxy esters are formed entirely from peroxide linkages, and in polyfunctional systems may then serve to effect condensation polymerization. This is thought to be one of the several most important "drying" mechanisms.

† Since this chapter was written, E. H. Farmer and his associates have begun the publication of new work on oxidation mechanisms [*Trans. Faraday Society*,

If the author has succeeded in dissipating some of the fog of uncertainty and complexity which surrounds the chemistry and physics of the stand oils and their films or has encouraged more extensive investigations within this field, he may be excused for such interpretations of the work of others as some may feel to have been unwarranted.

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## CHAPTER 5

### SYNTHETIC DRYING OILS \*

FRANCIS SCOFIELD

For many years attempts have been made to synthesize oils having drying properties. Van Heuckeroth (4) has compiled a summary of patents through 1935. Many of these products are of dubious merit and others are simply solutions of resinous materials. Of course, many resin solutions and some liquid resins show a strong resemblance to drying oils, and may be used in the same way. Such materials are outside the scope of this chapter, which is, rather arbitrarily, restricted to the esters of unsaturated fatty acids and polyhydroxy alcohols, usually glycerol.

In recent years, the development of these oils has been encouraged by the high price and shortage of tung and similar oils, and many patents covering these products are being issued all the time. New products are being developed so rapidly that a survey of the actual products being offered would very soon be out of date. Therefore, this article will be confined to a general discussion of the types.

Synthetic drying oils may be classified in three general groups:

1. Non-drying or semi-drying oils which have been treated to alter their structure and increase their ability to dry.
2. Oils synthesized from fractionated fatty acids.
3. Oils formed from fatty acids derived from petroleum and similar sources.

In addition, drying oils containing a catalyst which accelerates oxidation, or polymerization, or both, and oils obtained by fractionating the glycerides of drying or semi-drying oils to separate the better drying fractions are sometimes spoken of as synthetic drying oils.

The treatment of non-drying oils to alter their structure is exemplified in dehydrated castor oil (see Chapter 4, Volume I). Another

\* This subject is discussed in greater detail in Chapters 4 and 5, Volume I.

method with which considerable work has been done is the isomerization of oils such as soybean to conjugate the double bonds. Burr (2) has described the method involving alkali treatment, and Bradley and Richardson (1) have investigated it further. While Burr's method requires a non-aqueous solvent, Bradley and Richardson have shown that the reaction may also take place in the presence of water at suitable temperatures and pressures. They have described a method of determining the degree of conjugation by ultraviolet absorption and have shown that 30 to 50 per cent of the double bonds in fatty acids from linseed and soybean acids may be conjugated by suitable treatment.

The fractionation of fatty acids may be by means of vacuum distillation, molecular distillation, or solvent extraction. Suitable acids may then be re-esterified with glycerol to produce oils having the desired properties. Several oils of this type are commercially available.

The direct synthesis of fatty acids from petroleum derivatives is not yet a commercial process, but Drinberg (3) has described a number of drying oils made by this method. It is probable that, for some time to come, oils made by this method will be too high in price for commercial application.

The future development of synthetic oils appears to lie in a combination of the first and second types. No method has yet been developed by which the isomerization process can be made to go to completion, and, indeed, Bradley and Richardson show that when a highly conjugated oil, such as tung oil, is treated with alkali, the conjugation is reduced. It seems, therefore, that, in order to produce essentially pure conjugated acids, some form of fractionation as well as isomerization will be necessary.

The production of pure conjugated acids will make possible glycerides which are formulated to the requirements of the particular user, instead of requiring, as now, that the formulator adapt himself to the composition of natural oils. Specifically, the pure glyceride of 9-11, linoleic acid, should have most of the properties of tung oil, combined with the freedom from yellowing of soybean oil. Also such a development would enable us to utilize as drying oils such oils as soybean, cottonseed, and corn, which are most economically produced, rather than the rarer and more expensive oils which happen, in their natural condition, to approach more nearly the properties we desire.

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## CHAPTER 6A

### EFFECTS OF RESINS ON OILS \*

RALPH C. SHUEY

Oils as constructional materials are modified by admixture with other materials, in as great a measure as are steel, aluminum, and other structural materials by their admixtures. Traces of certain other substances produce marked changes in properties. A given oil properly processed with suitable resins may have its properties changed just as markedly as cast iron can be changed by proper processing with carbon, nickel, manganese, chromium, and other elements to produce the modern steels.

#### Heat Treatment

Two irons of the same carbon content may have altogether different physical properties due to methods of heat treatment and the consequent different state of the solution or dispersion of the contained carbon. In like manner two varnishes of the same oil and resin content may have little or no resemblance to each other because differences in heat treatment have produced altogether different properties. A particular heat treatment suitable for the best processing of the oil without admixture generally is unsuited for the best processing of the oil when mixed with other substances. The differences obtained (as with iron) may manifest themselves both in the working properties and in the service and endurance of the finished product.

An accurate evaluation of the effects of heat treatment on these oil mixtures is complicated by the changes and additions of other materials intervening between the final heat treatment and the formation of the film. Furthermore, many of the changes are of the

\* This chapter is a modified version of an article written by R. C. Shuey, appearing in *Industrial and Engineering Chemistry*, Volume 32, pages 921-930, July, 1940. The manuscript for this chapter was originally written for *Protective and Decorative Coatings* but was first published in this periodical. It is reprinted with the permission of the editor of *Industrial and Engineering Chemistry*.



irreversible type. A correlation of cause and effect is therefore more often inferential than direct.

The progress of the heat treatment of oils, often referred to as polymerization, may be followed by periodic observation of both the chemical and the physical changes. Polymerization, strictly speaking, is a specific term for a particular chemical change, and there is a question whether the term should be allowed to include the idea of physical changes of state such as change of particle size and gelation or solidification. A change from liquid to solid produced by a reduction in temperature certainly cannot be considered strictly a form of polymerization. Also under the heat in the kettle it may be possible to produce virtual solidification without the production of appreciable change in chemical properties detectable by such tests as iodine number determination (27, 28) and specific refraction (18).

The solution or dispersion of a resin in an oil, in the absence of other variables, produces changes in all the physical constants of the oils. It also often complicates determination of the chemical constants. In few cases is the value found to be that of the mathematical mean of the components. A systematic study of changes therefore generally must be based upon comparison with simpler or more definitely known cases supposed to have at least some measure of parallelism.

**Effects on Gelation.** Among the most apparent changes taking place during heat treatment is an increase in body or viscosity which may be continued to virtual solidification, especially with the more reactive oils. The addition of resins generally changes the rate of this "bodying," and, as different resins have various degrees of effect, it was thought desirable to establish some sort of zero point from which to evaluate the specific effects of the various resins.

The primary effect of addition might be considered to be simple dilution; therefore the addition of a simple diluent and a study of its effect on the course of the heat treatment would produce an idealized curve to serve as the zero point from which to evaluate changes.

Using tung oil, the most common quickly polymerizable oil, for study, soybean oil was chosen to serve as the "inert" diluent. Some work by Bolton and Williams (4, 5) indicated that in comparison to tung oil this oil polymerized so slowly that the amount of insoluble material produced on gelation of a mixture of the two oils is practically proportional to the tung oil content.

The Browne gelation test (7), with slight modification (22), was used to establish the curve of gelation of tung oil by running tests at

various temperatures from 392 to 662° F. (200 to 350° C.). Because of the chance of interference due to oxidation, parallel tests were also made in closed and sealed tubes. Both curves are shown in Fig. 1. It is apparent that at the low temperatures, where the time was long, oxidation produced acceleration, whereas at the higher temperatures oxidation appeared to produce slight retardation.

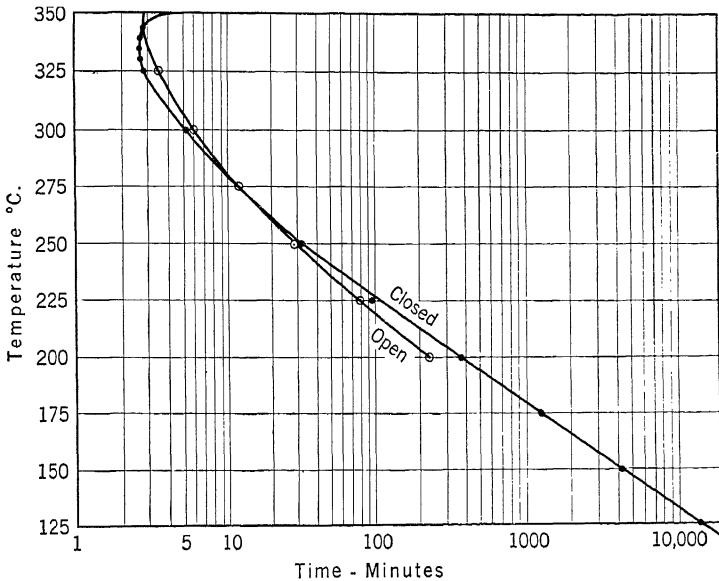


FIG. 1. Open and Closed Tube Gelations of Tung Oil.

The increase in gelation rate with increasing temperature is such that, roughly, the time is halved for each increase of 25° F. (13.9° C.) or quartered for each increase of 50° F. (27.8° C.).

For linseed oil there is a halving of the time for each 37½° F. (20.8° C.) of temperature increase. These values apply only through that portion of the curve which is approximately a straight line.

By repeating these determinations with tung oil diluted with 10, 20, 30, 40, and 50 per cent of soybean oil, equivalent curves were prepared which can serve as the framework of the gelation rates in the presence of the designated percentages of "inert" diluent. This is shown in Fig. 2.

At any given temperature, the change in gelation rate due to dilution can be calculated by a comparison of these values. At 392° F.

(200° C.) the formula for this rate change was calculated to be approximately:

$$T_{\text{mix}} = T_{\text{oil}} \left( \frac{1}{c} \right)^{1.7}$$

in which  $T_{\text{mix}}$  = Time required to gel the mixture.

$T_{\text{oil}}$  = Time required to gel tung oil.

$c$  = Concentration of tung oil in the mixture.

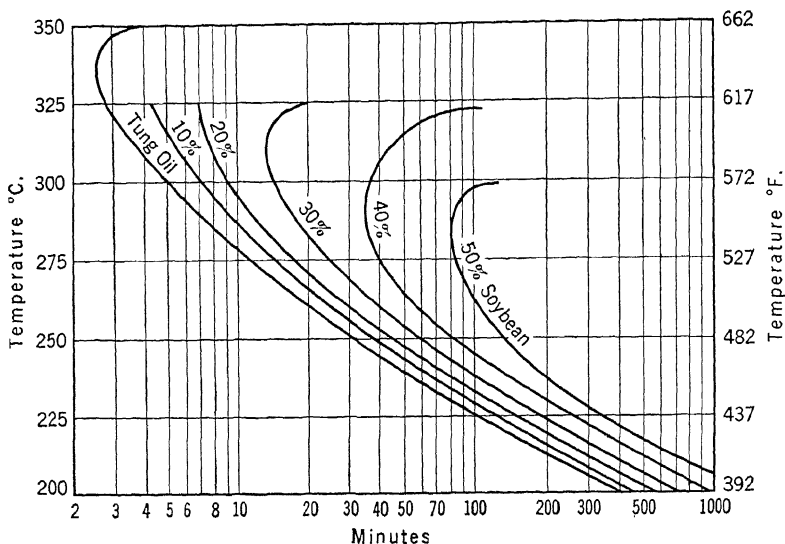


Fig. 2. Gelation Time of Tung Oil. Effect of Temperature and Dilution (Soybean Oil).

At higher temperatures the retarding effect was greater. With increasing dilution the temperature required to prevent gelation is lowered as shown by the upper portion of the lines becoming horizontal at lower temperatures.

Subjecting mixtures of tung oil and various resins to equivalent gelation tests gives values for the change in gelation rate due to these resins (23). Any marked departure from these values produced by an equivalent weight of resin under the same conditions may be considered as due to some factor other than simple dilution, and it is possible by comparing such departures to evaluate to a certain extent the different effects of various resins. For the sake of brevity only the values obtained at 482° F. (250° C.) will be discussed. They are shown in Fig. 3. Percentage of diluent (resin or other oil) is plotted

vertically, and gelation time horizontally. Considering the gelation rate of the oil used as unity, and dividing the gelation rate of the mixture by that value, was the device used for making all determinations comparable. This derived value is termed the gelation rate factor. This factor multiplied by 30 (an average gelation time for tung oil at 482° F. (250° C.)) gives comparable gelation times in minutes.

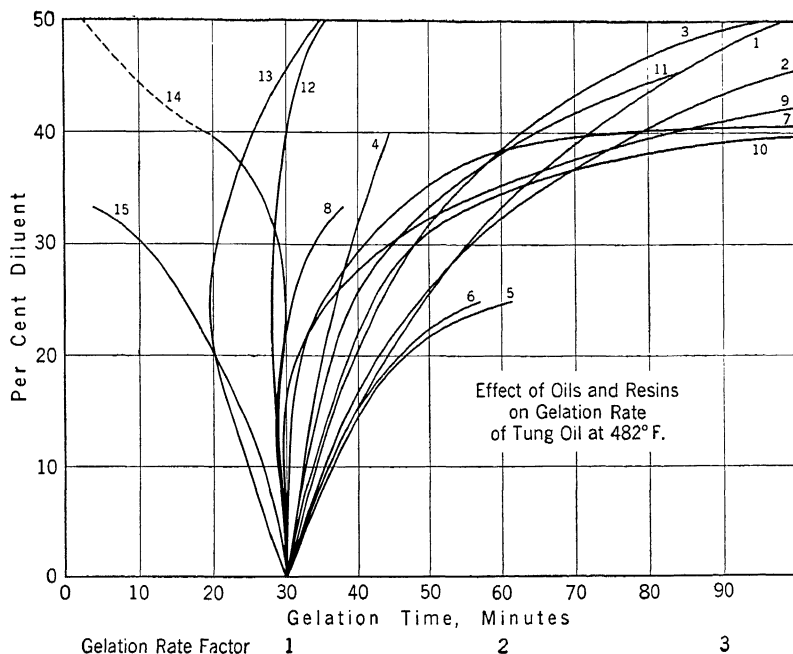


FIG. 3.

1. Dilution Formula  $(1/c)^{1.7}$  392° F. (200° C.)
2. Soybean Oil
3. Linseed Oil
4. Chlorinated Diphenyl
5. Rosin
6. Limed Rosin
7. Ester Gum
8. Congo.
9. Aliphatic Substituted Phenol Resin *A*
10. Aliphatic Substituted Phenol Resin *B*
11. Aliphatic Substituted Phenol Resin *C*
12. Polybasic Acid-Phenol Resin
13. Phenyl Substituted Phenol Resin
14. Heat Reactive Substituted Phenol Resin *D*
15. Heat Reactive Substituted Phenol Resin *E*

The formula referred to above as representing the effect of the dilution of tung oil with soybean oil or "inert dilution" at 392° F. (200° C.) is shown as curve 1, whereas the observed values for the same mixtures at 482° F. (250° C.) are shown as curve 2. The increase in retarding effect with increasing diluent content at the higher temperature is apparent. It is evident that increased temperature within certain ranges produces an effect similar to increased diluent content.

Linseed oil as a diluent is shown in curve 3. Having an appreciable content of linolenic glyceride, which is more easily polymerized than the linolein and olein of soybeans, it would be expected also to polymerize to a certain extent and thus give the effect of acceleration in comparison to the "inert" diluent.

Curve 4 represents chlorinated diphenyl as the diluent. This resin is supposed to have no effect on the polymerization of tung oil and therefore might be considered an "inert diluting resin." This resin appears to produce more relative acceleration than linseed oil. Such apparent increase may be due to various causes. For example, an increase in melting point and viscosity causes the test sample to be stiffer, with a consequent consideration that the mixture is gelled at an earlier stage in the actual polymerization of the oil. In other words, high-melting or very viscous diluents appear to produce the effect of premature gelation before polymerization has progressed to the same stage which is adjudged as "gelled" with a liquid diluent. This generalization is supported by a comparison of determinations on various lots of resins of different melting points at different temperatures. At lower temperatures this melting point effect is invariably accentuated.

Among the older resins commonly used with tung oil are rosin and limed rosin, shown in curves 5 and 6. Both these retard gelation markedly more than the previous diluents, so may be considered as producing actual retarding of the effect of heat on the tung oil.

Ester gum (Acid 6) shown in curve 7 produces more rapid bodying than any of the previous substances, whereas congo, curve 8, is still more rapid. It has been shown (10) that acid oils are definitely slower in bodying than the neutral glycerides. We have observed that rosin varnishes are definitely slower than ester gum varnishes. Now we find an acid material (congo) which produces faster bodying than the neutral rosin ester. There evidently is another factor in operation. The degree of dispersion of the resin appears to have an influence, the more coarsely dispersed materials producing less dilution effect per

unit of weight than the ones which are more nearly in solution. Reasoning of this sort is subject to the criticism that molecular weight determinations on colloidal materials are unreliable (19) and the apparent molecular weight is dependent largely upon the conditions of determination and may bear little relationship to the dispersion in another solvent or dispersant (2).

Among the straight phenol-aldehyde resins we find a greater spread in activity than in all other examined classes combined. An aliphatic substituted phenolic type (curve 9) shows an apparent retarding effect at 50 per cent resin ( $12\frac{1}{2}$ -gallon varnish), in which it is exceeded only by rosin and limed rosin. At 25 per cent resin (37-gallon varnish), however, it has a markedly faster rate than ester gum.

As this resin is not appreciably polymerizable by heat, this acceleration in long oil varnishes cannot be ascribed to resin polymerization being mistaken for oil polymerization. The fact that even at 450° F. (232.2° C.) its long oil varnishes are easily gasproofed, producing varnishes of excellent durability and high waterproofness and alkali resistance, indicates that normal oil polymerization or something akin to it has taken place.

Two other aliphatic substituted phenolic types (curves 10 and 11) show rates of the order of ester gum. The resins with the highest melting points (curves 9 and 11) show the more rapid rate; yet they show a distinct crossing at about 40 per cent resin. The one with the lowest melting point (curve 10) shows slower cooking rates at all concentrations. They are all exceptionally good at gasproofing tung oil. If cooked with tung oil at still higher temperatures, the resin of curve 11 maintains its rapid bodying rate whereas 10 and 9 lag markedly. The order of the drying times of the varnishes is the same as the order of the cooking rates at high temperatures even though the drying tests are made on varnishes cooked at 482° F. (250° C.) or below, resin 11 being the most rapid and 9 the least rapid. There appears to be some connection between proximity to the unity time (30 minutes) at 20 to 30 per cent resin and quick drying. These three resins impart remarkable exterior durability to tung oil even in short oil varnishes, a fact not true of the resins previously discussed and not true of many other types of "100 per cent phenolics."

The resin shown in curve 12 is a polybasic acid-phenol resin which changes the bodying rate of the oil but little irrespective of resin concentration. In fact, its tung oil varnishes can be cooked on the schedule of straight tung oil at any resin concentration up to 50 per cent and at any temperature from 450° F. (232.2° C.) up to the high-

est temperature at which the operator would have sufficient time to handle tung oil. It, however, does not impart as great a durability to the very short oil varnishes and is inferior to the previous three in gasproofing.

The phenyl substituted phenol resin shown in curve 13 starts toward the left (marked acceleration) and maintains this acceleration almost up to the 50 per cent concentration point. This is the most effective of all in the production of gasproofing, alkali resistance, and improvement of durability with increase in resin concentration.

The last two curves (14 and 15) represent two of the more active substituted phenolic resins of the heat-reactive type. The bend in these curves is in the opposite direction to all the others. As these resins polymerize with heat, any effect they may have on the oil is hidden by the polymerization of the resin reducing the apparent cooking time. At the higher resin concentrations this polymerization of the resin has reduced the solidification time to less than the time required to warm the 1-gram sample used to the temperature of the bath in which it is immersed. Because of the limited time available for heat treatment of the oil, gasproofing is difficult, and the indications are that the oil is essentially unchanged in this short time. Their greatest utility is in hardening the softer resins such as ester gum and limed rosin. When diluted with such soft or retarding resins, this type of resin can be held in the kettle sufficiently long and at sufficiently high temperatures to produce gasproofing, thus producing alkali resistance and durability improvement in proportion to the amount of phenolic resin used.

Generalizations are always dangerous, yet we may draw some fairly safe conclusions from this array of apparently discordant observations.

(1) Acceleration of gelation rate produced by a resin which itself is hardened by heat is not necessarily connected with an increase in the rate of polymerization of the oil with which it is cooked.

(2) Acceleration of the oil gelation rate by a resin which is not of the heat-hardenable type appears to be connected with acceleration of oil polymerization or a reaction similar to oil polymerization in effect. This seems a logical conclusion from the increased gasproofing and durability obtained in these cases. Further evidence will be presented later.

(3) The resins which show comparatively little increase in curvature with increase in resin concentration produce better drying varnishes when cooked at high temperatures than do the resins which produce marked curvature. (Curves 8, 11, 12, and under limited con-

ditions 13.) The proof of this lies in comparison of similar curves at higher temperatures.

(4) The change in gelation rate producible by an inert diluent is practically never produced by the varnish resins in common use. (Soybean oil and chlorinated diphenyl are the only observed cases of dilution producing a change in rate exponentially proportional to the reciprocal of the concentration of the tung oil.) Each of the commonly used resins, therefore, appears to exert some specific effect on the course of the bodying of the oil. For differentiation of these effects, confirmation must be looked for in a study of the other properties of the varnishes.

In considering resins as diluents, if consideration is given to the three factors—direction of curvature, degree of curvature, and location of the line with respect to tung oil under inert dilution—it is possible to form certain conclusions as to probable behavior of other oils as well as tung oil when bodied in the presence of these resins.

Turning for a moment to linseed oil, the gelation rate data of which under dilution are at present much more fragmentary, it has been observed that the resins which show but little increase in curvature with increased resin concentration (generalization 3 above) are most suitable for use with linseed oil either alone or in admixture with tung oil. They produce better drying and durability, the ones standing farthest to the left of the formula line (acceleration) showing the greatest durability and the ones to the right (retardation) the least.

Conversely, the resins showing the greatest curvature are the least suited for use with linseed oil (curves 5, 6, 7, 9, and 10). There is a possibility that this is connected with the observation that they produce poorer drying in varnishes cooked at the higher temperatures.

The question may be raised that, since varnish cooking is seldom carried to the gel point, gelation rate evaluations are beside the point. However, the Wurstaal test and the Browne test, both gelation rate evaluations, have been the accepted methods for the purpose throughout the history of the modern use of tung oil. In comparison let us examine the other most apparent changes during bodying.

**Viscosity Increase during Heat Treatment.** Both the string test and the finger test on a cold drop of the cook are modified viscosity tests. It is true that they are not subject to accurate numerical expression, but they are amenable to remarkably accurate duplication by a skilled operator desiring to reproduce a known cook accurately.

Viscosity determined on a chilled sample of an undiluted varnish by Gardner-Holdt tube, pipette, or other instrument is not necessarily



proportional to the viscosity which will be found on a sample of the same material after dilution to a given degree with a given solvent. Nor are viscosities in different solvents always related directly to each other (3). The type and degree of dispersion may change during dilution or storage. Viscosity determinations made during the cooking process on the material of the cook at the temperature of the cook do, however, give a measure of the physical state of the cook at that time. The change occurring during cooling or solution can thus be eliminated by making viscosity determinations in the kettle with any of the mechanical types of viscometers, such as the De Vilbiss or Brookfield, or even a pipette kept immersed to insure uniform temperature and simply withdrawn during the timing of the efflux. All three of these instruments have been used in collecting the data for the following discussion.

If tung oil is brought to a given temperature at the rate of  $10^{\circ}\text{ F.}$  ( $5.5^{\circ}\text{ C.}$ ) per minute, it can be shown by calculation from the data of Fig. 1 that the warm-up period is equivalent to a time between 4 and 5 minutes at that temperature. If the oil is held at that temperature and the viscosity determined periodically, a curve similar to that of Fig. 4 will be obtained, that is, the change in viscosity is approximately hyperbolic.

If, however, the points in Fig. 4 are plotted time versus log viscosity, they fall exactly on the lines shown as curve tung oil only of Fig. 5. Figure 4 was derived from the lines of Fig. 5 merely to illustrate why plotting arithmetically, as is generally done, fails to show the breaks in the curves as drawn in Fig. 5. Figure 5 is derived from the average of a number of determinations at various times on different oils by all three instruments. The only correction applied was to consider a viscosity of 200 centipoises at  $450^{\circ}\text{ F.}$  as complete gelation, arbitrarily scaling all determinations on a basis of complete gelation (200 centipoises) occurring in a corrected time of 66 minutes. This was done because the remainder of the curves were plotted from varnishes made from 66-minute oil.

Before endeavoring to interpret the observations on the varnishes of Fig. 5 we should endeavor to find the significance of the breaks in the oil or reference curve. Viscosities on the warm-up were calculated to  $450^{\circ}\text{ F.}$  from observations at the lower temperatures and are of doubtful value on that account. The line of no change in viscosity ends at about 20 minutes after reaching  $450^{\circ}\text{ F.}$  ( $232.2^{\circ}\text{ C.}$ ), which is the time at which the oil begins to become incompletely soluble in acetone on dilution of one volume to 20 with acetone. Insolubility in acetone

increases progressively throughout the next stretch, reaching a practical maximum at the break shown at 25 centipoises. At this point dilution in the same manner, but using mineral spirits in place of

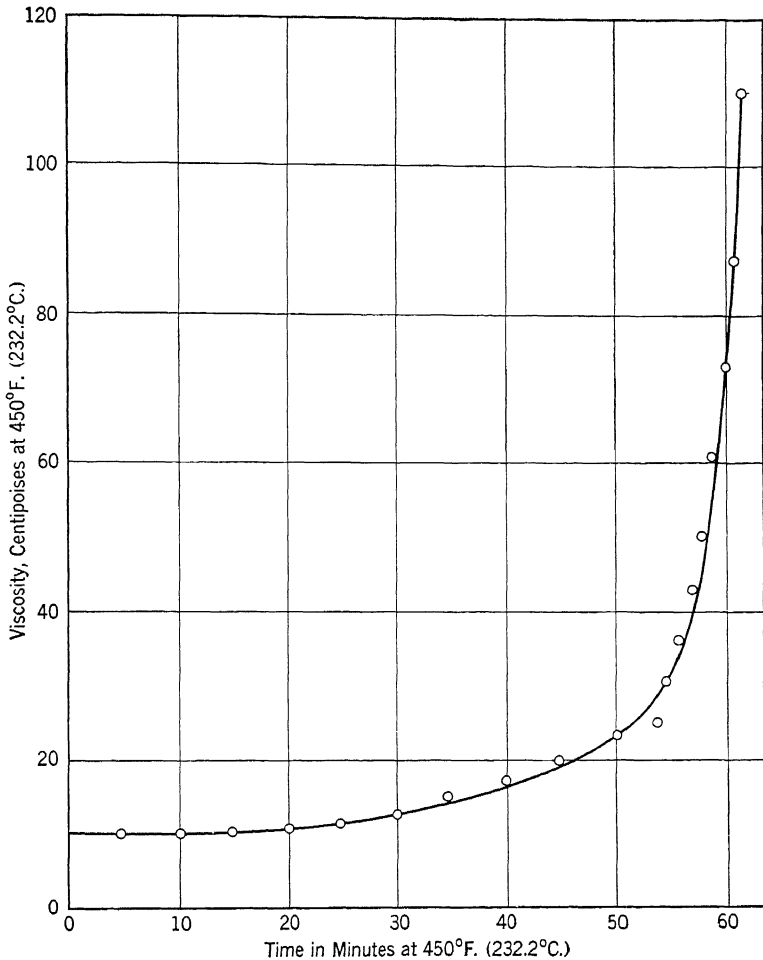


FIG. 4. Viscosity Increase of Tung Oil at 450° F. (232.2° C.).

acetone, begins to show a precipitate insoluble in mineral spirits. This progressively increases through the final stretch of the curve up to solidification. From 200 centipoises to solidification is a matter of a fraction of a minute. The 200 centipoises point for all practical purposes is identical with the end point of the Browne test. For purposes

of identification, the point at which the first material insoluble in mineral spirits appears will be called the mineral spirits point. The time required to reach this point is very close to 80 per cent of the time required to accomplish gelation, whereas the time of arrival at the acetone point is approximately 35 per cent of the gelation time.

It is not known why there should be no appreciable change in viscosity during the first 20 minutes at 450° F. (232.2° C.). There certainly is chemical change taking place, for nearly half the loss in

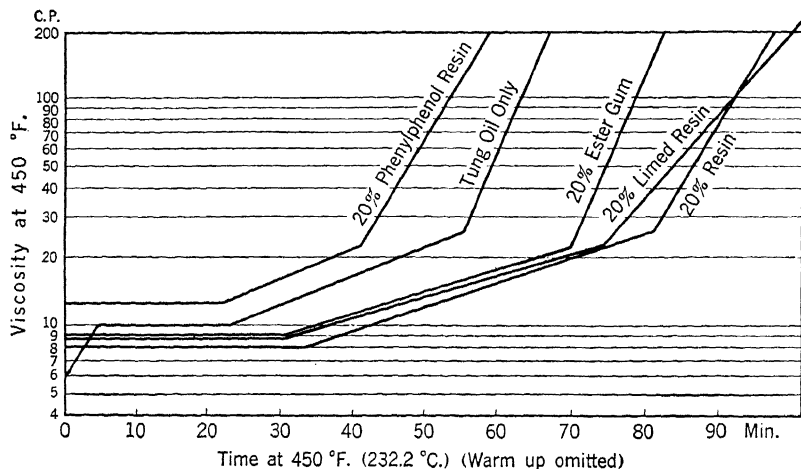


Fig. 5. Viscosity vs. Time at 450° F. (232.2° C.). Tung Oil and Its 50-Gallon Varnishes.

iodine number occurs during this time. Whatever the substance being formed, it must have a viscosity at that temperature very close to that of raw tung oil. The acetone-insoluble material definitely has a greater viscosity than tung oil. It appears to consist, at least to a great extent, of dimer.

The mineral spirits-insoluble portion appears also to be largely dimer (6, 17), at least insofar as the Diels-Alder type of reaction is involved, but in a different state of dispersion or aggregation. The break at the commencement of insolubility in mineral spirits coincides with the point of string from the spade as determined by the practical varnish maker. Naturally, the presence of a resin (which would be solid when cold) advances the string point because of its presence in the oil, thus allowing the varnish maker to anticipate the reaching of this point before the cook progresses into the stage of "false body" or what we may call "dispersed gel." Viscosity determination at kettle

temperature can thus be used for numerically recording the progress of a cook and estimating arrival at the desired end point.

Turning to the cooks containing 20 per cent resin, we see that curve 1 of Fig. 5 represents the viscosity changes when the resin is rosin; curve 2, limed rosin; curve 3, rosin ester or ester gum; and curve 4, a phenyl substituted phenol resin. By comparison with the curves for these resins in Fig. 3 it is apparent that there is some relationship between the gelation test and the progress of the viscosity change. The phenyl substituted phenol resin, which produced marked acceleration in the gelation test (Fig. 3), owes this acceleration more to advancement of the mineral spirits point in the viscosity curve than to an increase in the formation of what has been designated as dispersed gel. In fact the dispersed gel (mineral spirits point to gelation) portion of the curve has a more gentle slope than has tung oil alone, that of the phenyl substituted phenol varnish being practically the same as that of rosin ester varnish at this concentration.

This leads to the conclusion that both these resins have equivalent holding power against the formation of dispersed gel and possibly to the deduction that the acceleration of the former is due to a speedier reaction in the zone between the acetone point and the mineral spirits point. The acetone point is essentially unchanged in the presence of 20 per cent of phenyl substituted phenol resin whereas the meager data at hand indicate that it has been delayed in the presence of the other resins.

It is worthy of note that the phenyl substituted phenol resin varnish becomes gasproof at the acetone point at 450° F. (232.2° C.). Whereas the other varnishes and tung oil have to be carried beyond the mineral spirits point at this temperature in order to pass the same gas-checking test. The optimum of serviceability of the phenyl-phenol resin varnishes occurs at the acetone point (24), whereas for best service the others must be cooked at sufficiently higher temperatures to bring the gasproofing point at or to the left of the mineral spirits point. This leads to the conclusion that the production of acetone-insoluble material in the phenyl substituted phenol resin varnish is neither necessary nor desirable, but that the production of acetone-insoluble material is required in the case of the other varnishes. Presumably, then, the acceleration of reaction has taken place before reaching the acetone point.

**Chemical Polymer Formation.** Since no dependably comparable determinations of iodine numbers could be made on varnishes containing the resins, we are forced to rely on a comparison of viscosity values

and iodine numbers of the oil only for any inferences as to possible chemical significance in this difference in behavior. Such a comparison is shown in Fig. 6 with the iodine number values inverted for the purpose of superimposing loss of iodine number and gain in viscosity. A comparison of the progressive acetone and mineral spirits tests of

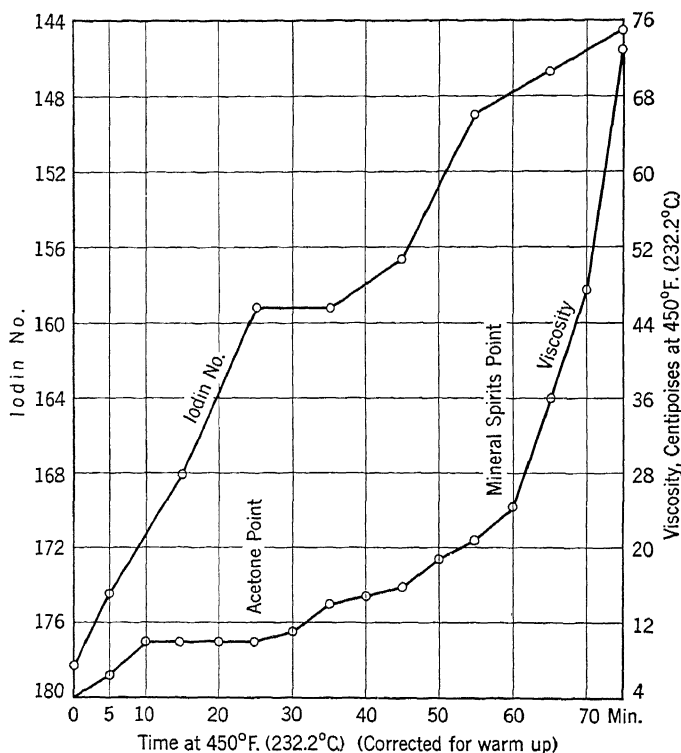


Fig. 6. Comparison of Iodine Number Decrease and Viscosity Increase of Tung Oil, Bodied at 450° F. (232.2° C.).

tung oil and its 50-gallon phenyl substituted phenol resin varnish is given in Fig. 7. It is noted that approximately half the loss in iodine number occurs before arrival at the acetone point (no appreciable viscosity change) and almost 90 per cent of the iodine number loss has occurred upon arrival at the mineral spirits point (25 per cent of the viscosity change), leaving only 10 per cent of the iodine number change to take place during 75 per cent of the viscosity change shown. Virtual solidification took place during cooling of the last sample.

If iodine number loss is considered evidence of primary valence polymerization, then half this polymerization has taken place without appreciable change in viscosity or without the formation of a sub-

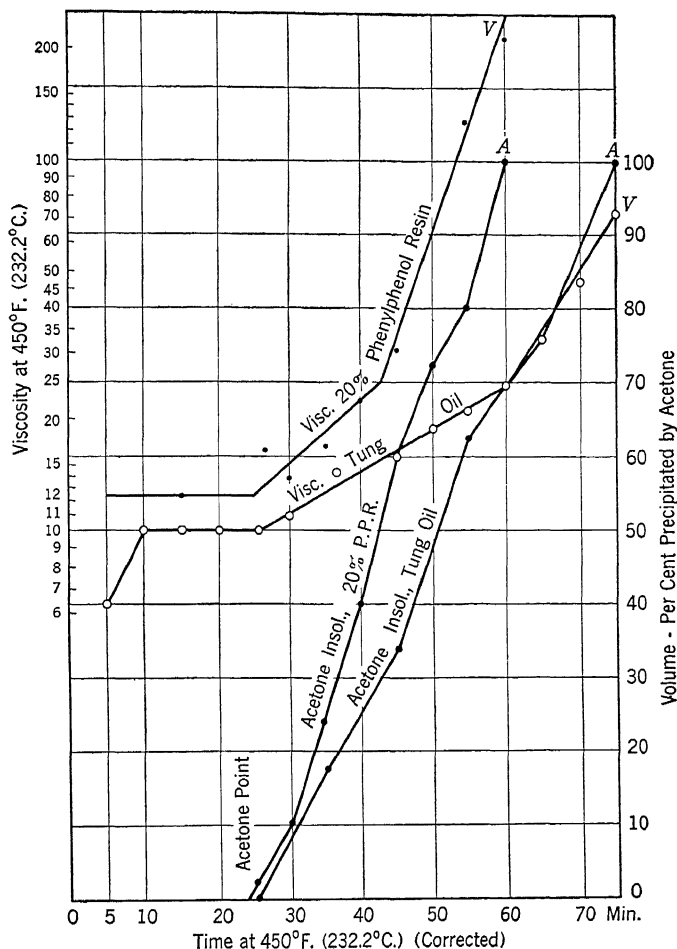


Fig. 7. Increase in Viscosity and Acetone Insolubility of Tung Oil and Its 50-Gallon Varnish Made with Phenylphenol Resin.

stance insoluble in acetone, whereas only 10 per cent of the chemical polymerization is accomplished during the 75 per cent increase in viscosity conveniently described as formation of dispersed gel. Steger and Van Loon (19) have shown that loss in iodine value is not directly proportional to the loss of double bonds; also (20), that there is no

sudden change in chemical composition during gelling. Marcusson (13) concludes that the solid and liquid polymers are chemically identical.

But aside from the consideration of such reasoning we have the observation that at the point of only half the iodine number change the phenyl substituted phenol resin has effectively gasproofed the oil. This indicates that the component responsible for gas checking has disappeared. Varnishes stopped at this point show durability in service has surpassed that normally producible in other varnishes only on effecting the omitted changes by continuing the cook until practically 90 per cent of the iodine number change has been accomplished.

### Application Properties

**Consistency and Solubility.** Oils cooked only to the acetone point require but little dilution to bring them to brushing consistency. If cooked to the mineral spirits point, oils will stand dilution to 45 or 50 per cent non-volatile to obtain brushing consistency. Most resins show very low viscosities when diluted to 50 per cent with appropriate solvents.

No general rule can apply to oil-resin mixtures under dilution, for the choice of end point, the type solvents used, and the effects of driers and other added materials must all be taken into account. A rosin or limed rosin varnish bodied on the down heat may be carried to the mineral spirits point or slightly beyond to obtain the maximum amount of thinner addition. Raising the melting point of the rosin or limed rosin by fusing it with the heat-reactive type of substituted phenolic resin produces some additional body and thus allows for equivalent dilution without passing the mineral spirits point of the oil. Conversely, varnishes stopped at the acetone point or slightly beyond may require only 35 per cent of volatile to bring them to brushing consistency, thus producing 140 per cent as much film at the same covering rate per gallon. In this case two coats would be practically equivalent to three coats of the varnish cooked to the mineral spirits point, thus saving the cost of one application.

The choice of solvents, simply from the standpoint of economy, often centers around the use of the maximum amount of mineral spirits. If all components are infinitely soluble in mineral spirits, it may be the sole diluent, although brushing properties are generally improved by some turpentine or dipentene. The former being an active oxygen carrier is preferred for varnishes requiring the maximum of oxidation for film formation; the latter is indicated in varnishes which require

the minimum of oxygen intake or are extremely sensitive to oxidation.

If a component or reaction product is not soluble in mineral spirits, some strong active solvent of the aromatic class is indicated; or, if higher non-volatile is desired for a given cook and viscosity, increasing the percentage of strong solvents will generally produce a certain reduction in viscosity.

**Solidification and Drying.** The so-called drying of an oil in the absence of a solvent is simply a change from the liquid to the solid phase. The change from liquid to solid may be adjudged to have taken place as soon as the percentage of solid phase has increased to the point where it has absorbed all the liquid phase and become rigid enough to display solid film properties. As colloids age, they lose their liquid-holding properties, so that, if the solid phase ages faster than the liquid phase disappears, we may observe sweat-back or after-tack. Sweat-back is the true syneresis, squeezing out of excess liquid with the aging of the film if the film contains large quantities of liquids such as oils high in stearin and olein which do not solidify with age.

After-tack may be defined as slow solidification of a certain liquid portion which lags behind the main film-forming substance but finally does solidify and become a part of the solid film.

Resins, being solids at room temperatures, are true film formers just as much as the polymerized portions of the oils. Normally the addition of resins thus increases the percentage of solid phase. Low-melting resins or resins liquefiable by a relatively small percentage of liquid are generally of comparatively low value as film formers because of their tendency to accentuate the after-tack and sweat-back in the film as it ages, especially under warm or humid conditions. High-melting resins and especially those resins having great liquid absorption properties are therefore preferable. This assumes the greater importance of the present-day use of the softer oils, which contain too high a percentage of liquid component to display quick drying. The use of additional resin to speed up hardening tends to make the film become brittle as the liquid phase slowly solidifies. Chemical combination of oil and resin is preferable to simple solution as a means of preventing syneresis in high liquid phase films.

Oils held for any appreciable time above the temperature of maximum gelation rate, as shown in Figs. 1 and 2, have their non-solidifiable portion increased, and so are slow drying with a tendency toward tackiness. This maximum rate temperature is apparently lower with tung oil and higher with perilla than with most of the other oils. For best drying, therefore, the indicated temperatures should not be



exceeded. The practice of bodying the slower oils in the absence of resins, adding the resins on the down heat, is an attempt to avoid this slow drying.

As mentioned in the discussion of Fig. 3, resins differ greatly in the effect produced by increased concentration. In general increased temperatures produce effects similar to increased concentrations. The polybasic acid phenol resin (curve 12 of Fig. 3) should, therefore, produce exceptional drying of the slower oils at all concentrations, even when high temperatures are used. This is borne out in practice.

The mechanism of solidification has not been completely worked out. It is generally conceded, however, that both polymerization and oxidation reactions are involved and that the relative rates of these vary greatly with temperature as well as other conditions. Solidification by baking is largely polymerization. At room temperatures oxidation assumes greater importance, particularly in compositions that require a considerable degree of oxidation to activate the final stages of polymerization. However, some oxidation products of oils are liquids and overoxidation (sometimes called maloxidation) acts as a retardant. Since the oxidation products are less durable and less resistant to chemical attack than the polymerization products, oxidation should be held at a minimum by the use of the lowest adequate amount of driers.

Rapid oxidation, especially as a stimulant to polymerization in accordance with the chain reaction theory of Stephens (21) and others, produces quick drying, but if oxidation does not cease when the film is dry, premature aging by oxidation and ultimate destruction of the film will ensue.

### **Effect of Heat Treatment and Resins on Service Behavior**

**Chalking versus Checking.** No satisfactory correlation of adhesion and durability has been worked out, perhaps more because of other conflicting factors than because of inability to measure adhesion forces accurately. For example, shrinkage takes place (increase in density in addition to oxidation-volatilization losses) during the aging of oil films and, if the film becomes too rigid, cracking or checking must perforce ensue. If tensile strength exceeds adhesion strength, cracks may be few. On the other hand, for a given shrinkage the pull exerted where a crack does form will be proportionately greater, and, as the surface of most films is slightly harder than the interior, slight slippage tends to result at the interface with the substrate producing alligatoring, or the coating curls away at the cracks producing peeling. If the

tensile strength of the film is low, a multiplicity of cracks will form and, if the cracks are numerous enough, they may be so fine as to evade detection with the unassisted eye, producing virtual failure of the whole film before they are apparent. If the multitudinous cracks are only superficial and the body of the film retains its integrity, this effect is often called chalking, and no particular harm has been done to the protective value of the film. Superficial chalking then would appear preferable to checking, and checking preferable to peeling.

Most oleoresinous films have much more adhesion strength than is required for good service. They are far superior in adhesion to such films as straight nitrocellulose.

Although nitrocellulose alone displays poor adhesion on many surfaces, the addition of plasticizers (liquids which distend the film and reduce its tensile strength) and resins (which have good adhesive properties) has successfully overcome this objection. If peeling or curling is to be guarded against, addition of a distending liquid (preferably a film former and not a liquid plasticizer) should reduce the tensile strength to a value commensurate with the adhesive strength. Similar results have been obtained by the cooking in of linseed oil with tung oil varnishes which otherwise would have had tensile strengths many times the required tensile strength and therefore far in excess of the more than adequate adhesive strength (24). The addition of the more flexible oils for this purpose may be complicated by a slowing of the drying rate of the varnish unless a resin is used which will produce quick drying even when these oils are used in comparatively high percentages.

Films composed of resins which are themselves resistant to oxidation do not shrink excessively so that addition of such resins to oils in the making of varnishes should proportionately reduce both checking and peeling if the oils are properly processed. The phenyl substituted resins, and to a lesser extent some of the other phenolic resins, have this property and therefore greater durability can be imparted to their short oil varnishes than can be obtained in their long oil varnishes, which are in turn more durable than the oils themselves or other varnishes made from these same oils (8, 15). Most resins, especially those of the retarding and low gasproofing class, reduce the durability of their short oil varnishes markedly below that of their longer oil varnishes.

**Toughness, Tensile Strength, Elasticity, Elongation, and Flexibility.** These properties can hardly be treated separately because of their

interrelation. Toughness and tensile strength are generally associated, as are elasticity, elongation, and flexibility, although very viscous liquids may display elongation without elasticity.

The oils themselves when dried to films tend to have high elongation and comparatively low tensile strengths. In 27-gallon varnishes Nelson (14) has shown the following values:

Composition	Elongation, %	Tensile Strength, Kg./Sq. Cm.
Ester gum-tung oil	100	62
Limed rosin-tung oil	42	52
Limed rosin-linseed oil	88	28
Kauri gum-linseed oil	80	30

which can approximately be compared to 33-gallon varnishes of phenylphenol resin varnishes of the same age (5 hours at 212° F. (100° C.) (24).

Composition	Elongation, %	Tensile Strength, Kg./Sq. Cm.
Phenylphenol resin-tung oil	81	212
Phenylphenol resin-75% tung oil-25% linseed	82	158
Phenylphenol resin-50% tung oil-50% linseed	113	98
Phenylphenol resin-25% tung oil-75% linseed	102	63
Phenylphenol resin-100% linseed oil	91	10

These clearly indicate the lower tensile strength of linseed oil compared to tung oil and the softening effect of rosin, even though hardened with lime, when compared to the other resins. It also shows the enormous tensile strength of the phenylphenol resin-tung oil varnish and the high tensile strength combined with high elongation of equivalent varnishes at half linseed and half tung oil. It is unfortunate that a straight linseed oil film could not be made commensurate in aging time with the above values, but 7½ hours at 260° F. (126.6° C.) was necessary to obtain a film which could be handled and measured. At this age the values of varnish films were: (25)

Composition	Elongation, %	Tensile Strength, Kg./Sq. Cm.
Bodied linseed oil only	36.8	12.6
95% linseed oil-5% phenylphenol resin	56	17.3
80% linseed oil-20% phenylphenol resin	82.7	54

In the first series drier quantities commonly used for tung oil varnishes were used; in the second series larger quantities of driers more suitable for linseed were used.

After the varnish films had aged 100 hours at 260° F. (126.6° C.) plus 160 hours at 302° F. (150.0° C.), the values had changed to:

Composition	Elongation, %	Tensile Strength, Kg./Sq. Cm.
Bodied linseed oil only	3.35	290
95% bodied linseed oil-5% phenylphenol resin	7.4	275
80% bodied linseed oil-20% phenylphenol resin	7.8	320

thus maintaining the same elongation or flexibility relationship with age and giving numerical expression to the frequently observed high flexibility of these varnishes in practice even when compared to the oil itself.

**Oxidation.** As previously mentioned, oxidation, after film formation is complete, tends to become film destruction (11, 16). This is evidenced by increase in acid number in the film and subsequent loss of weight through the formation of volatile products. Some resins tend to increase the oxygen intake of oil films; others may retard it. As far as observed, all resins appear to retard the commencement of the loss in weight stage, possibly because dilution of the oil with resin gives a measure of physical interference with the ingress of oxygen and egress of the oxidation products.

Films of bodied oils and varnishes, with identical heat treatment containing identical driers and no volatiles, were spread at the same weight per unit area. (Weighed quantities in small tin cans spread completely over sides and bottom by rotation until set.) Previous experiments had shown that longer cooking would give lower oxygen

absorption values, but we desired to keep the viscosity of all varnishes low enough for spreading without the use of volatiles. The changes in weight with time were recorded for a period of nine months. Exposure was under indirect sunlight in a room free from laboratory fumes. Figure 8 shows graphically the weight changes observed with

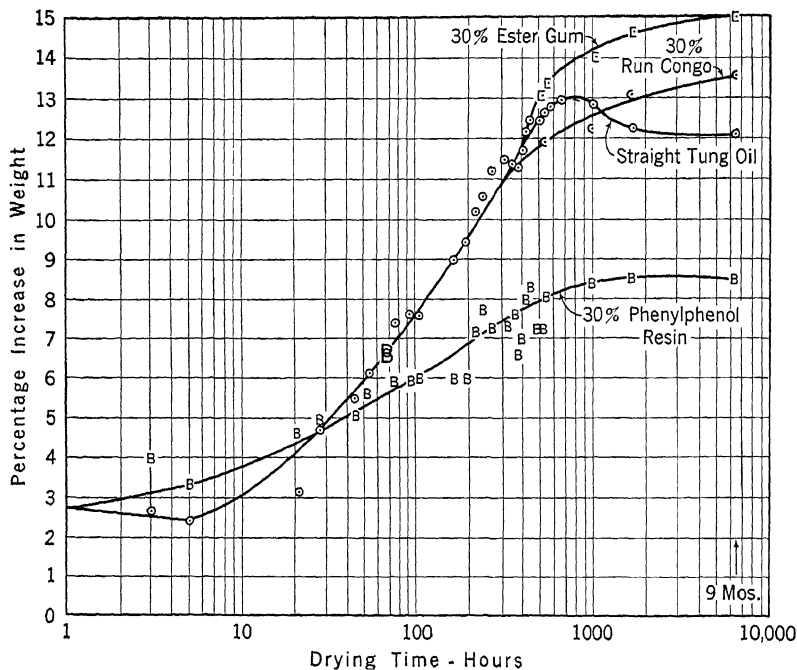


FIG. 8. Oxygen Absorption. Weight Changes in Films during Drying Tung Oil Varnishes (Added Drier in Solution), Cooked 30 Minutes at 400° F. (204° C.).

tung oil cooked 30 minutes at 400° F. (204° C.), and Fig. 9 the values with linseed oil cooked 30 minutes at 540° F. (282° C.).

Tung oil alone reached a peak at 13 per cent increase in weight in about 800 hours, or 1 month, dropping back to about 12 per cent in the following 8 months. The inclusion of 30 per cent ester gum during the bodying gave an essentially identical percentage change (calculated on the oil component) during the first 2 weeks, but continued to increase to a maximum of 15 per cent at the end of 9 months. Thirty per cent congo under similar conditions also departed from the oil line in about 2 weeks, but rose more slowly to 13½ per cent at the end of the experiment.

Thirty per cent of phenylphenol resin stimulated weight increase during the first day, but retarded it thereafter to hold the maximum down to  $8\frac{1}{2}$  per cent in 2 months, with no later change. Repeated experiments verified this first increase (a plausible explanation of quick drying) as well as ultimate lower intake under all cooking conditions

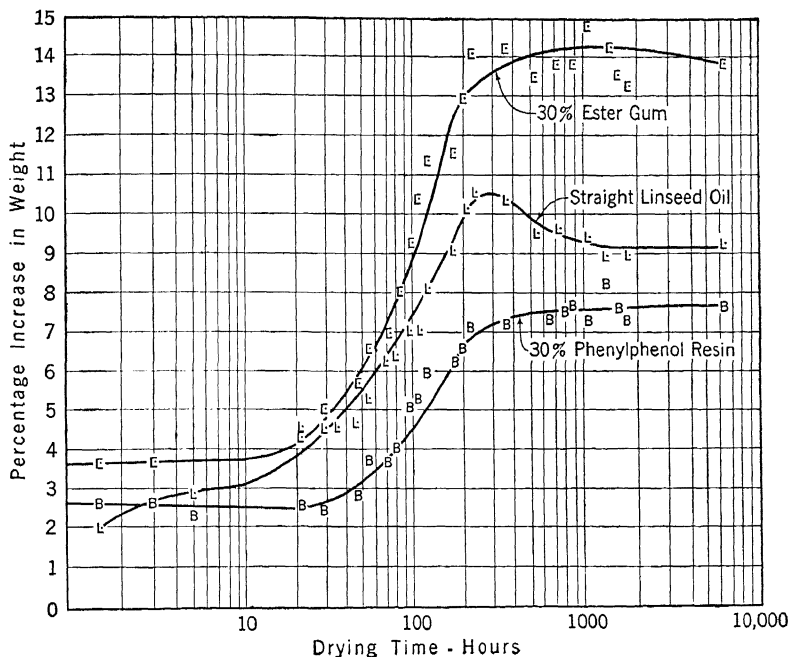


FIG. 9. Oxygen Absorption. Weight Changes in Films during Drying Linseed Oil Varnishes (Added Drier in Solution), Cooked 30 Minutes at  $540^{\circ}\text{F}$ . ( $282^{\circ}\text{C}$ ).

and at all concentrations of this resin. The lowering of the weight increase per unit of oil was found to be proportional to the amount of resin used, reaching the low value of only about 2 per cent total weight increase at 50 per cent resin, or a  $12\frac{1}{2}$ -gallon varnish.

Confirmation of this observed resistance to the effects of oxidation was also found in the determination of the acid number of varnish films exposed to the weather, the acid number of the phenylphenol varnish remaining essentially unchanged in 9 months, whereas the other varnishes showed increases of several hundred per cent.

Linseed oil alone reached a peak of  $10\frac{1}{2}$  per cent in about 12 days, dropping back almost to 9 per cent at the end of 9 months. Thirty

per cent ester gum gave a more rapid rise to over 14 per cent in about a month with slight indication of loss by 9 months. Thirty per cent phenylphenol resin, on the other hand, held back the weight increase to practically  $7\frac{1}{2}$  per cent in 2 weeks, with no change thereafter. This probably has direct bearing on the greater flexibility retention indicated by the elongation values.

**Solid-Liquid Phase Changes.** Long (11, 12) *et al.* have studied the gradual reduction in liquid phase during the aging of linseed oil films, concluding that loss of absorbed liquid phase is the direct cause of loss of flexibility and production of embrittlement with age. This is believed applicable to the other oils as well.

The addition of a hard resin normally reduces the proportional amount of liquid phase, consequently lowering the flexibility. The kauri reduction test is based on this effect. However, cooking in of Kauri gum does not produce the same embrittlement as is produced by the same amount of kauri added as a cold cut solution. The colloidal dispersion or phase distribution appears to be influenced favorably by the heat treatment. Zanzibar resin is reputed to stand above all others of the natural resins in this production of favorable effect by heat treatment. However, time appears essential in the development of this property so that, in the days of the use of zanzibar and linseed oil for marine varnishes, long-continued cooking of the oil with the resin was accepted practice.

Choice of resin, resin percentage, and heat treatment thus can all be utilized in modifying the properties of oil films. For rubbing varnishes, hard resins added at the end of the cook tend to produce rigidity and the comparative brittleness required for easy sanding. To increase the toughness of the varnish, having resin present during a greater percentage of the heat treatment generally favorably modifies the phase distribution and reduces the brittleness. For the maximum of toughness and flexibility, a resin of high oil or liquid phase absorption, present throughout the heat treatment, is the accepted practice. If the resin retards oxidation, as indicated by the weight increase curves, this should tend to prolong the flexible life of the film. Combinations of oils and resins displaying sweat-back (low liquid phase retention) would make for the poorest flexibility retention with age. For marine and other services requiring the maximum of toughness, those resins should be chosen which display the greatest freedom from sweat-back, perhaps the surest easy criterion of high liquid phase holding ability.

**Chemical Resistance and Weather Resistance.** Many relations between physical properties of films and their ability to stand weathering are apparent. The relation between chemical properties and weathering are often less apparent, for the films are practically never soluble in the chemical substances to which they are exposed.

Moisture absorption of the film, allowing the ingress of gases and chemicals, through their solubility in water, might be considered the most important link between physical properties and chemical effects; the exclusion of water practically excluding all commonly occurring deleterious substances not themselves soluble in the film.

As the vegetable oils have a certain measure of moisture-absorbing and -transmitting ability, one of the functions of resin is to control this water absorption. The U. S. Forest Products Laboratory (26) found the percentage efficiency in resisting moisture penetration to be:

3 coats of linseed oil .....	17%
3 coats of spar varnish (supposedly tung oil, resin unnamed) .....	60%
3 coats of rubbing varnish (supposedly tung oil, resin unnamed) .....	89%

which indicated the low value of the oil and the increase in protection produced by the resin. A rubbing varnish, high in resin, because of its physical characteristics would be the least durable of the three under exposure, but this early work indicated the high moisture-excluding value of resins compared to oils.

The problem then becomes one of obtaining the maximum of water resistance without loss of the physical properties requisite for maximum durability—in other words, the use of the maximum amount of resin consistent with the greatest freedom from checking and peeling. For marine service, the resins which are the best preventives of sweat-back are therefore again indicated.

The vegetable oils, being saponifiable oils, form soaps or salts with basic substances even when in the polymerized state. Many of these soaps are water soluble. On the other hand, dilute acids tend to cause the splitting by hydrolysis of the glycerides to fatty acid and glycerol. It is here that freedom from water absorption has great value in excluding the destructive chemicals. The use of an alkali resistance test in evaluating chemical resistance of varnish films is based much more on measurement of resistance to moisture than on measurement of the saponifiability of the oils. There is no question as to the saponifiability of the oils; it is simply a question of whether the alkali



has an opportunity to get to the oils to do its work. There is a probability that many chemists have failed to see the significance of this distinction.

Chemical effects are often accelerated by exposure to sunlight, but, unless the resin itself is deleteriously affected by sunlight, the reactions on the oil, most of them hydrolytic, will still be retarded by the exclusion of moisture.

Superficial chalking as distinguished from checking and the deeper forms of film failure thus appears to be related to the moisture-excluding value of the film for, with the practical effect of water confined to the exterior, a film of proper colloidal construction should have the weathering effects limited to the surface of the film only. In some cases the chalking thus produced may be removed by the elements. In most cases, however, where high gloss is desired, occasional washing or wiping is necessary for the purpose of removing accumulated grime, and the chalking is generally removed with the grime.

### Utilization of the Newer Oils

This discussion has been based principally on tung oil and linseed oil, because they are the most commonly used oils, and more data are therefore available. However, much of the discussion is equally applicable to oiticica, dehydrated castor, fish oil concentrates, soybean, and many others. The approximate composition of these oils is known (9), and proper blending to obtain equivalent colloidal effects offers no problem, especially if resin effects as well as oil properties are given full consideration.

The heat treatment required by the different oils is dependent principally on their composition. It is essential in any case that each oil be polymerized in the kettle to its optimum point; otherwise the solid-liquid phase relation will be out of balance during both application and service.

Resins which assist oil polymerization (essentially vertical type, Fig. 3) are preferably added at the commencement of the cook. There is often a definite advantage in bodying the slower oils in the presence of such resins, adding the faster oils later, so that both oils will profit by the beneficial effects of the resins and reach the optimum point simultaneously.

Oiticica oil contains approximately the same amount of polymerizable components as tung oil, but approximately 12 per cent of fats of the stearic acid class as compared to 4 per cent in tung oil. The satu-

rated or nearly saturated fats, which may be present as mixed glycerides (1), may or may not be crystallizable in the raw oil. As the unsaturates polymerize, however, their ability to hold the saturated fats appears to decrease and the portions which were originally effective as plasticizers become some of the worst offenders in producing the syneresis effects evidenced as sweat-back and brittleness. Oiticica thus requires plasticization to reduce or delay embrittlement with age. If plasticized with the slower oils, the percentage of saturated fats is seldom reduced, so that the tendency toward after-tack is increased without much permanent reduction in aging effects. Experience has shown that plasticization is best accomplished by the use of resins of high liquid phase retention, such as the phenylphenol type. These resins, if properly cooked in, not only preserve the flexibility of oiticica films but permit the use of as much as 50 per cent of the slower oils without significant reduction of drying time or appreciable loss of required film characteristics.

Dehydrated castor oil is practically free from saturated acids but lacks conjugated acids of the quickly polymerizable type, therefore requires speeding up. Dehydrated castor oil and oiticica together, in many properties, resemble an equivalent mixture of linseed and tung. Rosin and ester gum tend to produce too soft a film with such a combination. Much better drying is accomplished by the use of the resins giving essentially vertical lines in Fig. 3, after-tack being greatly reduced if not eliminated.

Recently fractionation of fish oil has been commercially accomplished, producing either bodied or unbodied oils containing only the unsaturated portions. The natural percentage of saturates in fish oil may be of the order of 25 or 30 per cent. Cold pressing may be used to reduce it to about 16 per cent. These new products, however, consist essentially of the higher molecular weight unsaturated portions separated from the non-drying and semi-drying components by fractional distillation or fractional precipitation. They therefore produce hard films because of lack of plasticizing fractions. Although clupanodonic glyceride is more highly unsaturated than eleostearic glyceride, the lack of conjugated bonds prevents these oils from drying as rapidly as tung oil. Mixed with tung oil they can be made to dry faster and harder than tung oil.

These oils are not subject to sweat-back, as are fish oils, but may display some after-tack because of the low degree of conjugation and lack of chain reaction stimulation during drying. If the high curvature resins are used, they should be added after bodying is accom-

plished. Best results are obtained, however, by the vertical and minimum curvature types, which will give better drying and flexibility retention on aging.

This discussion has been limited to treatment of oils by heat bodying, as influenced by the presence of resin, omitting many types of finishes containing oil which are not directly related to the routine processing of oils by polymerization.

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## CHAPTER 6B

### EFFECT OF OIL-REACTIVE ESTER RESINS ON CONJUGATED AND NON-CONJUGATED DRYING OILS

WILLIAM H. BUTLER

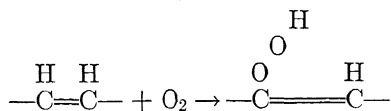
One of the more recent developments in resins for protective coatings is the oil-reactive type of ester resin based on acids such as bicycloheptenedicarboxylic acid. The chemistry of formation of the liquid resin esters is analogous to the alkyd resin reaction in the initial formation of the low polymer ester resin. The resulting ester resin is a potentially reactive intermediate which when heat-processed with conjugated or non-conjugated drying oils will copolymerize with the oil to yield a viscous liquid reaction product. This product polymerizes rapidly on further heating or air-drying. Resins of this type have been produced commercially for the past three years, and great impetus has been given to their use because of the scarcity of the conjugated drying oils, such as tung oil. The oil-reactive ester resins are produced as relatively low polymer intermediates which are compatible with such drying oils as linseed, soybean, fish oil, and other drying oils. When processed together under heat they result in a copolymer which makes possible the production of a wide variety of new processed drying oils. Such oils possess the properties of chemical resistance, rapid conversion to dry films, and oxygen stabilized coatings. Films based on soybean oil and the liquid resin copolymer show no change in flexibility, that is, they do not become brittle or sticky, when exposed in the oxygen bomb at 158° F. for a period of 8 to 14 days, or exposure to high humidity. A further indication of the reactive group in the ester resins is their adaptability to cross-linking with sulfur to produce flexible, solvent-insoluble gels. The reaction of these resins can be divided into two steps: first, the primary ester formation yielding a low polymer; second, the reaction in which the intermediate polymer is coupled by heat-processing with film-forming or other materials to produce the copolymer. During this second step the oil-reactive ester resin loses its chemical identity and the original raw materials cannot be separated by chemical analysis.

The chemical reactions involved in this secondary reaction may be considered as follows:

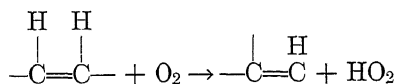
### Gelation of Linseed Oil Films

There is a mass of material on the chemical changes which take place when linseed oil or other conjugated or non-conjugated drying oils are converted by heat or oxidation from liquids to gelled masses or to dry films. There is, however, still no specific agreement as to the exact chemical changes. Within reasonable limitation there is agreement that these drying oils are converted from monomers to polymers in the final stages of drying. The time rate of conversion and extent of polymerization and the physical properties of the polymer are the factors which determine their use as coatings. The rate of reaction or conversion from liquids to dry solids or polymers is usually constant for the different drying oils. The rate is influenced by ultraviolet light and catalysts such as the metallic driers, peroxides, and other chemical substances.

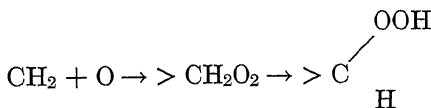
There has been considerable technical data as to the chemical changes which take place in polymerizing linseed oil. A discussion by Professor E. K. Rideal (3) on Dr. Bowles' thesis, "A study of the gelation of polymerized linseed oil films in the presence of cobalt," sheds some light on the chemical reactions involved prior to polymerization. It is considered that it can be taken for granted that one of the main first products of oxidation in the cure of the unsaturated esters was a hydroperoxide. Of the actual mechanism by which the first process took place there was very little knowledge at all. One could write a reaction of this type:



There are a number of variants. One that has been proposed was



A second method of approach was with the  $\text{CH}_2$ , and that rearranged itself as follows:



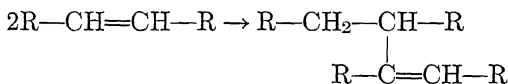
The next step after the hydroperoxide formation was extremely complicated. In the presence of catalysts the hydroperoxide went over to ketones, and these underwent further oxidation to acid and aldehyde. The next step in this reaction was the formation of the polymer. It could not be said that the polymer which was formed in the drying of linseed oil was necessarily a series of chains joined by chemical covalent linkage, or whether it was a polar aggregation of molecules. Therefore, Professor Rideal did not think it was possible to conclude from Dr. Bowles' experiments that he was necessarily dealing with a chemical polymer, but it could be said that we were dealing with a chain reaction and it was necessary to find out whether the chain produced was one of discrete molecules or a series of polymers.

Another type of mechanism for polymerization of drying oils has been advanced by Powers, Overholt, and Elm (2). Their conclusions are:

Five steps in the drying and ageing processes are discernible. The first step is the period of induction before oxidation is appreciable; the second step is the period where oxidation occurs most rapidly; this is followed by a third step where the oxygen apparently rearranges forming conjugated systems if they are not already present; the fourth step is polymerization accompanied by a rapid increase in density, a rapid decrease in specific refraction and a rapid drop in iodine value; and the fifth step, the aging step which occurs more slowly.

The fourth step is described as follows:

The activated double linkages may then enter into polymerization reactions according to the following scheme, which is known to be operative in the vinyl type of polymerization.



This mechanism readily explains the increase in density and the decline in specific refraction with little or no change in oxygen content during the second or polymerization step of the drying process.

Other evidence has also been presented that drying oils polymerize through reactions of the Diels-Alder type (1) during heat-bodding.

### Copolymerization and Gelation of Oil-Reactive Ester Resins and Drying Oils

The previous paragraphs indicate several probable reactions of linseed oil in its conversion from a monomer to a polymer and the chemical reactions which are involved. The mechanism of the poly-

merization of the linseed oil alone is a factor which must be considered in the reaction of the copolymer. Polymerization data were determined on both the conjugated oils and the non-conjugated oils and with the oil-reactive ester resins by two methods.

(1) The polymerization apparatus as described by Turkington, Shuey, and Butler (4) involves polymerizing a 2½-gram sample in a test tube in a bath held at a constant temperature. This apparatus is used with conjugated oils.

(2) A 2-gallon batch is run in a stainless steel kettle, and samples are removed over the period of heat-processing until a non-fluid gel is obtained. Samples are removed at intervals and tested for viscosity, acid number, drying rate, and chemical analysis.

For the purpose of these tests, two types of oil-reactive ester resins were chosen with the following specific properties:

	OIL-REACTIVE ESTER RESIN <i>A</i>	OIL-REACTIVE ESTER RESIN <i>B</i>
Acid number . . . . .	45-60	3-8
Solid content . . . . .	100%	100%
Color . . . . .	* Not darker than 2-L (Hellige)	* 1 + (Hellige)
Viscosity . . . . .	* 250-550 kv	* 500-800 kv
Specific gravity . . .	* 1.025-1.035	* 1.038-1.040

\* Reduced 3 resin to 1 toluol.

Oil-reactive ester resin *A* is a type which will polymerize on air-drying or baking to yield a hard solvent-resistant flexible coating. Oil-reactive ester resin *B* is a type which will heat-polymerize to a flexible gel but will not yield a dry coating.

The reaction of the oil-reactive ester resin with a conjugated oil such as tung oil shows that the time rate of polymerization is independent of the polymerization of the oil-reactive ester resin. The following data are the basis of this conclusion.

The two types of oil-reactive ester resins were polymerized at 250° C. Resin *A* polymerized to a solid in 18 minutes and resin *B* in 40 minutes. The low polymer resin *A* was then mixed with tung oil in the proportion of one part resin to two parts tung oil. The time for polymerization to a solid gel was 10 minutes at 250° C., while resin *B*, which was slower in heat-polymerizing than resin *A*, polymerized with the same proportion of tung oil in 5 minutes. The tung oil used in the test had a polymerization rate of 27½ minutes at 250° C. The copolymer reaction of resin *A* with tung oil accelerated the polymerization as compared to tung oil alone by 63.5 per cent, and resin *B*



accelerated the reaction by 81.7 per cent. For this reason, it is stated that the polymerization of the copolymer is independent of the heat-polymerization of the oil-reactive ester resin. Further data show that when the oil-reactive ester resin is reduced to 20 per cent with tung oil the same reaction time is obtained and there is no observable dilution effect.

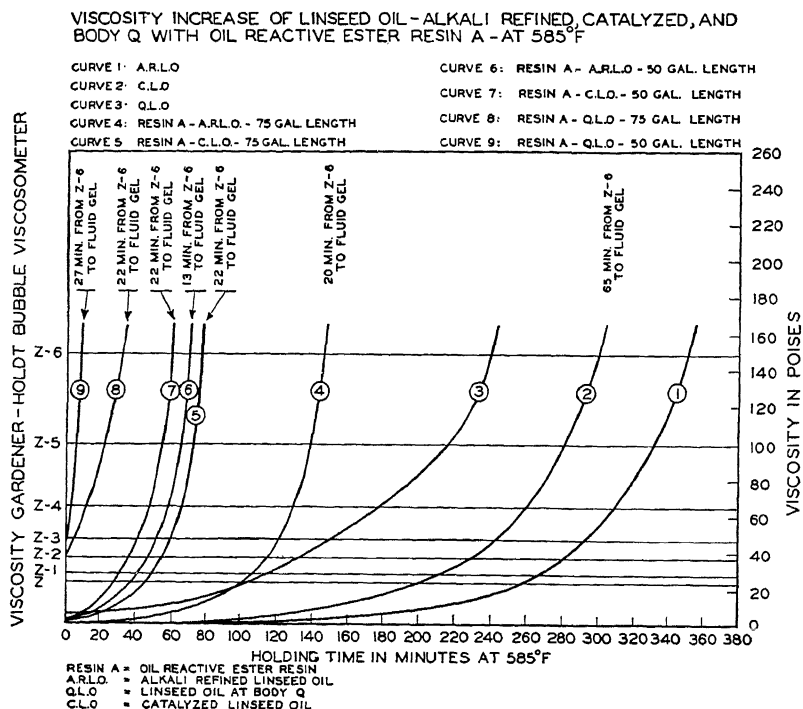


FIG. 1.

The reaction of these ester resins with a non-conjugated oil such as linseed is shown in Fig. 1. The curve for viscosity increase and final gelation was plotted from the samples which were removed at various intervals during the period of processing at 585° F.

It will be noted that the oil-reactive ester resin materially reduces the normal induction period for the linseed oil to reach a viscosity of Z- to Z-1, and the time from Z- to Z-1 to final gelation is also materially accelerated. A further analysis of these data shows that curve 9, which is based on 20 per cent of ester resin and 80 per cent of Q linseed oil, reaches a viscosity of 148 poises in 7 minutes at 585° F.; 15.1 per

TABLE I

Oil-Reactive Ester Resin A Q Linseed Oil at 540° F.				Oil-Reactive Ester Resin A Q Linseed Oil at 585° F.				Oil-Reactive Ester Resin A Alkali-Refined Linseed Oil at 560° F.				Oil-Reactive Ester Resin A Alkali-Refined Linseed Oil at 585° F.				Alkali-Refined Linseed Oil at 585° F.			
Time at 540 °F.	Visc. in Pouises	Acid Value	Sp. Gr.	Time at 585 °F.	Visc. in Pouises	Acid Value	Sp. Gr.	Time at 560 °F.	Visc. in Pouises	Acid Value	Sp. Gr.	Time at 585 °F.	Visc. in Pouises	Acid Value	Sp. Gr.	Time at 585 °F.	Visc. in Pouises	Acid Value	Sp. Gr.
....	7.27*	6.82*	0.964*	...	9.26*	7.0*	0.968	...	0.844*	4.2	0.918*	...	0.803*	4.5*	0.947	...	0.426*	0.6*	0.926
0'	12.52	...	...	0'	36.05	...	0.971	0'	0.903	...	...	...	1.39	...	...	...	0.403	0.5	...
10'	17.52	...	...	10'	63.02	...	...	...	...	...	...	...	...	...	...	...	...	...	...
15'	20.75	...	...	...	...	...	...	15'	1.65	...	...	...	2.27	...	...	...	...	...	...
20'	26.50	...	...	20'	87.30	7.2	0.972	...	...	...	...	...	...	...	...	...	...	...	...
30'	31.50	6.8	0.965	30'	141	...	...	30'	2.13	...	...	...	...	...	...	...	...	...	...
40'	40.50	...	...	40'	223	7.9	...	...	...	...	...	...	4.43	4.8	0.959	...	...	...	...
45'	43.60	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
50'	49.60	7.0	0.966	50'	406	8.3	0.977	...	...	...	...	...	6.95	...	...	...	1.11	...	...
60'	59.80	...	...	55'	Fluid	Gel	Hot	100'	2.87	...	...	...	...	...	...	...	...	...	...
75'	80.10	...	...	...	...	...	...	...	4.60	...	...	...	15.63	...	...	...	...	...	...
90'	112	6.3	0.968	...	...	...	...	...	6.53	4.1	9.60	...	43.10	...	...	...	2.69	...	...
120'	277	...	...	...	...	...	...	...	...	...	...	...	188	6.0	0.978	...	...	...	...
135'	Visc.	Gel.	Hot	...	...	...	...	...	10.82	...	...	...	170'	Fluid	Gel	Hot	...	...	...
150'	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
170'	...	...	...	...	...	...	...	...	17.50	...	...	...	...	...	...	...	...	...	...
180'	...	...	...	...	...	...	...	...	38.85	...	...	...	...	...	...	...	...	...	...
210'	...	...	...	...	...	...	...	...	63.00	...	...	...	...	...	...	...	17.60	...	...
240'	...	...	...	...	...	...	...	...	173	4.0	0.973	...	...	...	...	...	...	...	...
270'	...	...	...	...	...	...	...	...	Fluid	Gel	Hot	...	...	...	...	...	...	...	...
285'	...	...	...	...	...	...	...	285'	...	...	...	...	...	...	...	...	...	...	...
300'	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	50.15	...	...
330'	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	100	...	...
360'	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	3.55	4.2	0.965

Note: \* Dispersion at 440° F.

cent of ester resin and 84.9 per cent of Q linseed oil (curve 8) reaches a viscosity of 148 poises in 33 minutes and final gelation over an additional period of 22 minutes; and the Q linseed oil (curve 3) requires 235 minutes at 585° F. to reach a viscosity of 148 poises. The corresponding acceleration in viscosity increase to 148 poises is 97 per cent for the 20 per cent resin copolymer and 86 per cent for the co-

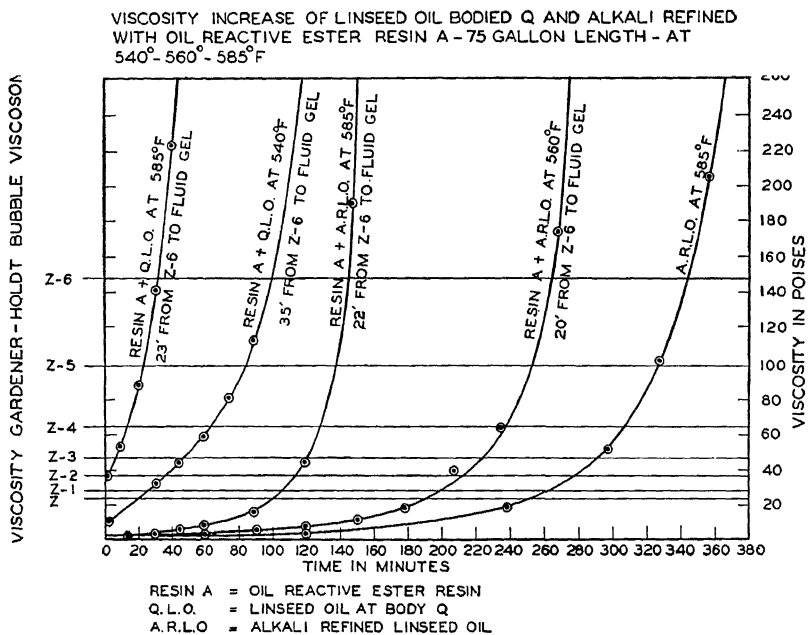


FIG. 2.

polymer containing 15.1 per cent ester resin. The rate of acceleration closely parallels the results obtained with the conjugated oils. Similar acceleration is obtained with other non-conjugated oils such as soy-bean, fish, and perilla oils.

Additional data on the viscosity increase of the copolymer based on oil-reactive ester resin A diluted to 75-gallon length (15.1 per cent resin-84.9 per cent drying oil) are shown in Table I and Fig. 2. Table I also shows the relative change of acid number, viscosity, and specific gravity over the period of heat processing.

Comparison of the data in Table I and Fig. 2 indicates the following conclusions:

1. The acid value of the copolymer decreases when heat-processed at 540° F. and 560° F. and shows a slight increase when heat-processed at 585° F.

2. The specific gravity of the copolymer increases during heat-processing.

3. Acceleration in viscosity increase and polymerization is obtained on heat-processing the copolymer over a temperature range of 540° F., 560° F., and 580° F.

Table II covers the data on the viscosity increase at 560° F. with oil-reactive ester resins *A* and *B*.

TABLE II

Oil-Reactive Ester Resin	Polymerization Time with C.W.O. at 250° C.		Viscosity Increase with Linseed Oil at 560° F.—75-gal. Length			
	12½ gal.	25 gal.	Time at 560° F.	Resin <i>A</i> (Poises)	Resin <i>B</i>	Linseed Oil Alone
<i>A</i>	12' 0"	11' 0"	0	D (1.00)*	D-E (1.00-1.25)	A- (0.50-)
			1 hr.	K (2.75)	M-N (3.20-3.40)	C (0.85)
			2 hr.	U (6.27)	T (5.50)	G (1.65)
			3 hr.	Y (17.60)	V (8.84)	N-O (3.40-3.70)
			3½ hr.	Z-2 (36.20)		
<i>B</i>	4' 10"	5' 0"	4 hr.	Z-4 (63.40)	Y (17.60)	U-V (6.27-8.84)
			4½ hr.	Z-6 + (148.0+)	Z-1 (27.0)	
			5 hr.	25 min. to fluid gel.	Z-2-Z-3 (36.2-46.3)	Y (17.60)
			5½ hr.		Z-4-Z-5 (63.4-98.5)	
			6 hr.		Z-6 + (148.0+)	Z-1 + (27.0+)
					30 min. to fluid gel.	
			7 hr.			Z-3 (46.30)
			7½ hr.			Z-4 (63.40)

\* Letters are Gardner-Holdt scale designation, and numerals are poise values.

The same acceleration is noted both with the conjugated and non-conjugated oils, but comparison of these results with Fig. 1 will indicate that a preliminary heat-processing of the oil alone either helps to remove an inhibitor present in the oil or the copolymer reaction is changed because of the partial polymerization of the linseed oil.

#### Acetone Dilution Tests of Oil-Reactive Ester Resins Processed with Linseed Oil and Linseed Oil Alone

A method had previously been suggested by R. C. Shuey (5) covering the acetone dilution of heat-processed oils and resins in order to determine the percentage of acetone insoluble fraction. The acetone

dilution was determined by diluting 5 cc. of the heat-processed resin and oil with 45 cc. of acetone and then determining the insoluble portion after settling for 48 hours. These data are covered in Table III.

TABLE III

Ester Resin A—75-Gal. Length at 560° F.			Ester Resin B—75-Gal. Length at 560° F.			Linseed Oil Alone at 560° F.		
Time at 560° F.	Viscosity in Poises and G.H.	Acetone Dilution, % Insoluble	Time at 560° F.	Viscosity in Poises and G.H.	Acetone Dilution, % Insoluble	Time at 560° F.	Viscosity in Poises and G.H.	Acetone Dilution, % Insoluble
440° F.	0.84 C	None	560° F.	1.14 D-E	None	560° F.	0.29 A-	None
560° F.	0.96 D	None	1 hr. 560° F.	3.37 M-N	10	1 hr. 560° F.	0.825 C	None
1 hr. 560° F.	2.87 K	10	2 hr. 560° F.	5.51 T	24	2 hr. 560° F.	1.88 G-H	None
2 hr. 560° F.	6.53 U	30	3 hr. 560° F.	8.94 V	40	3 hr. 560° F.	3.53 N-O	30
3 hr. 560° F.	17.49 Y	60	4 hr. 560° F.	16.80 Y	60	4 hr. 560° F.	7.36 U-V	60
3½ hr. 560° F.	38.85 Z-2+	80	4½ hr. 560° F.	25.6 Z-1	70	5 hr. 560° F.	15.28 Y	80
4 hr. 560° F.	63.16 Z-4	84	5 hr. 560° F.	40.3 Z-2	78	6 hr. 560° F.	31.55 Z1+	96
4½ hr. 560° F.	173.0 Z-6++	100	5½ hr. 560° F.	79.6 Z-4	85	7 hr. 560° F.	46.6 Z-3	100
			6 hr. 560° F.	153 Z-6++	100	7½ hr. 560° F.	64.7 Z-4	100

The data show that the linseed oil heat-processed at 560° F. has a higher percentage of acetone insoluble at equivalent viscosity than has the copolymer.

#### Properties of Air-Dried Films from Heat-Processed Oil-Reactive Ester Resins and Linseed Oil with Comparisons against Other Resins in Equivalent Dilution

The water resistance of air-dried films composed of the copolymer of linseed-oil-reactive ester resin is compared in Table IV with similar films of oil alone and of oil processed with other resins. The composition was 84.9 per cent drying oil to 15.1 per cent resin to give an oil

length of 75 gallons. The heating was conducted at the temperatures noted in the table and held until viscosities stated in column 3 were obtained. All samples were reduced to viscosity E with mineral spirits and driers added equivalent to 0.015 per cent cobalt, 0.015 per cent manganese, and 0.05 per cent lead, calculated on the weight of solids. The varnishes were applied on glass test tubes by dipping and then permitted to air-dry for 8 days. The tubes were then immersed in water for 6, 24, 48, and 72 hours as noted in Table IV. The "viscosity

TABLE IV

Sample No.	Composition of Sample	Viscosity of Solids in Poises	Water Resistance of Films After Aging 8 Days			
			6 hours	24 hours	48 hours	72 hours
1	ES. RES. A—QLO at 540° F.	28.45	O.K.	O.K.	Sl. haze	Sl. haze
2	"	40.60	O.K.	O.K.	V. sl. haze	V. sl. haze
3	"	55.80	O.K.	O.K.	O.K.	O.K.
4	"	83.60	O.K.	O.K.	O.K.	O.K.
5	O.S. PHEN. RES.—QLO at 540° F.	37.1	O.K.	O.K.	Sl. haze	Sl. haze
6	"	82.5	O.K.	O.K.	Sl. haze	Sl. haze
7	MOD. PHEN. RES.—QLO at 540° F.	34.9	O.K.	Sl. haze	V. hazy	V. hazy
8	"	57.8	O.K.	Sl. haze	Haze	Haze
9	"	70.7	O.K.	O.K.	V. sl. haze	V. sl. haze
10	MOD. ALK. RESIN—QLO at 540° F.	38.9	Sl. haze	Sl. haze	V. hazy	V. hazy
11	"	59.6	V. sl. haze	V. sl. haze	Haze	Haze
12	"	71.3	O.K.	V. sl. haze	Haze	Haze better than 11
13	Ester Gum QLO at 540° F.	29.8	V. sl. haze	Haze	V. hazy	
14	"	44.1	V. sl. haze	Sl. haze	V. hazy	V. hazy
15	"	49.5	V. sl. haze	Sl. haze	V. hazy	V. hazy
16	"	67.3	V. sl. haze	Hazy	V. hazy	V. hazy
17	QLO alone at 540° F.	35.1	O.K.	O.K.	Sl. haze	Sl. haze
18	"	51.3	O.K.	O.K.	V. sl. haze	V. sl. haze
19	ES. RES. A—RLO at 585° F.	4.43	O.K.	O.K.	Sl. haze	Sl. haze
20	"	15.63	O.K.	O.K.	O.K.	O.K.
21	"	43.10	O.K.	O.K.	O.K.	O.K.
22	ES. RES. A—QLO at 585° F.	27.62	O.K.	O.K.	O.K.	O.K.
23	"	36.05	O.K.	O.K.	O.K.	O.K.
24	"	63.02	O.K.	O.K.	O.K.	O.K.
25	"	87.03	O.K.	O.K.	O.K.	O.K.
26	ES. RES. A—RLO at 560° F.	17.49	O.K.	O.K.	O.K.	O.K.
27	"	38.85	O.K.	O.K.	O.K.	O.K.
28	"	63.16	O.K.	O.K.	V. sl. haze	V. sl. haze
29	RLO at 585° F.	17.16	O.K.	O.K.	Hazy	Hazy
30	RLO at 585° F.	50.15	O.K.	O.K.	V. sl. haze	Sl. haze
31	Dehydrated Castor Oil	52	O.K.	O.K.	O.K.	O.K.

ES. RES. A = Ester Resin A

O. S. PHEN. RES. = Oil-Soluble Phenolic Resin

MOD. PHEN. RES. = Rosin-Modified Phenolic Resin

MOD. ALK. RES. = Rosin-Modified Alkyd Resin

QLO = Body Q Linseed Oil

RLO = Alkali-Refined Linseed Oil

Sl. = Slight

V. sl. = very slight

TABLE V

Sample No.	Film Hardness as Determined by Swinging Beam. The Values Are Reported in Seconds										Resin and Temperature	
	Hardness of Film After Air-Drying											
	4½ hr.	6 hr.	8 hr.	24 hr.	48 hr.	72 hr.	96 hr.	168 hr.	504 hr.	804 hr.		1848 hr.
1	29-30	32-33	30-33	23-36	23-23	23-23	23-23	23-23	23-23	20-23	39-39	ES. RES. A—540° F.
2	33-36	30-30	29-33	29-26	23-20	23-23	23-23	23-23	20-26	26-26	33-36	"
3	32-33	33-36	25-28	26-26	20-20	20-20	20-20	20-21	20-23	20-26	36-36	"
4	32-29	36-33	33-31	23-23	20-19	20-20	20-22	20-21	20-20	26-26	33-33	O. S. PH. RES.—540° F.
5	Wet	Wet	Wet	Wet	23-23	26-29	26-28	33-32	40-38	46-44	57-58	"
6	Wet	Wet	Wet	Wet	23-23	23-23	26-27	26-20	30-32	53-53	56-59	MOD. PH. RES.—540° F.
7	Wet	13-16	14-14	16-16	13-13	20-16	23-23	22-23	36-34	53-56	66-62	"
8	Wet	13-14	13-13	13-10	13-13	13-16	23-23	23-23	36-36	53-56	75-70	"
9	10-10	13-14	13-12	13-10	13-13	19-16	26-25	20-20	36-36	56-56	65-66	MOD. ALK. RES.—540° F.
10	Wet	Wet	10-12	13-13	13-13	16-16	28-28	28-28	46-46	59-59	66-65	"
11	Wet	Wet	10-11	10-10	10-10	16-16	27-33	27-33	46-46	56-66	69-79	"
12	Wet	Wet	10-14	13-13	13-13	16-16	23-23	23-23	36-33	46-46	62-59	Isater Gum 540° F.
13	Wet	10-13	14-13	13-13	13-13	16-16	23-23	23-21	36-33	46-46	60-50	"
14	Wet	10-10	9-10	13-10	10-10	15-15	23-24	25-22	38-39	56-53	66-62	"
15	Wet	6-9	8-9	13-12	10-12	13-13	23-24	25-22	40-40	56-56	66-62	"
16	Wet	13-14	11-11	10-13	13-13	13-13	20-20	20-20	40-39	53-53	59-56	"
17	Wet	36-33	37-37	33-29	26-26	20-20	23-23	25-26	23-26	20-19	23-23	QLO—540° F.
18	30-29	29-36	33-34	33-29	23-23	23-23	23-22	23-22	20-20	16-16	23-21	"
19	36-36	33-33	30-32	30-29	26-26	23-33	33-33	36-25	35-33	29-26	39-39	ES. RES. A—585° F.
20	36-33	29-28	30-30	29-29	23-22	26-26	26-26	26-26	27-29	26-23	33-33	"
21	33-35	39-34	30-31	26-23	20-20	23-23	25-22	24-22	23-23	26-26	32-33	"
22	29-29	29-30	32-31	30-30	23-23	26-25	26-27	24-22	26-26	26-26	33-36	ES. RES. A—585° F. QLO
23	29-27	30-31	30-29	26-26	20-20	23-23	23-23	23-23	26-26	26-26	33-33	"
24	29-28	33-29	23-26	26-26	20-20	20-20	23-24	23-23	21-23	23-20	33-26	"
25	25-27	29-27	26-27	26-23	20-20	23-20	23-23	23-23	20-21	23-23	30-33	"
26	42-39	33-34	27-28	29-26	20-23	26-26	33-33	32-35	26-26	26-26	33-36	ES. RES. A—590° F. RLO
27	36-27	32-30	29-32	20-26	26-27	26-23	24-26	25-22	21-20	26-26	33-33	"
28	37-39	29-29	28-29	26-26	23-26	24-24	23-23	23-23	20-20	23-26	29-30	"
29	39-36	35-39	30-36	39-36	29-27	26-26	26-25	26-26	20-20	26-23	23-26	"
30		32-33	43-39	33-29	26-26	23-23	20-20	20-20	20-22	19-26	25-26	RLO—585° F.
31	85-82	85-70	73-72	60-59	52-52	43-43	45-45	45-45	32-36	33-30	30-32	Dehyd. Castor Oil

of solids in poises" in the third column is the viscosity of the heat-processed material prior to reducing with solvent.

The film hardness of the air-dried coatings as described under Table IV was tested as follows: Varnishes at viscosity E were flow-coated on glass plates and the hardness of the films was determined at stated intervals, using the Gardner-Holdt swinging beam. The hardness values were reported as soon as the film was sufficiently set and hard to permit a reading. The first interval reported, however (4½ hours), somewhat exceeded the set time for a number of the films. The hardness values on this apparatus ranged from 0 seconds to approximately 300 seconds, which is the hardness of the glass. At a reading of 25 seconds the films were set and firm, but varied in the degree of surface dryness. In reference to surface dryness, the copolymer films all showed very much better surface dryness than the heat-processed oils, but this does not show up in the hardness values.

It will be noted in Table IV that the oil-reactive ester resin when copolymerized with linseed oil improves the water resistance of the films and in this respect is superior to the other resins listed. In Table V, it will be noted that a quick set or air-dry is obtained and that the films retain the stabilized hardness over an extended period. As previously noted, the hardness tests do not show the effect of surface dryness and in this respect the copolymer is considerably better than the other processed oils listed.

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## CHAPTER 7

### HEATING METHODS

JOSEPH JARES

Selection of suitable heating equipment for cooking of oils and varnish ingredients should be made with an appreciation of the fact that the value of results sought must be measured by the quality and overall cost of the finished product and not merely by the unit cost or consumption of a given fuel. The real problem is to use such source of heat energy and equipment as will produce the best overall results under specific manufacturing conditions.

Any method of selection based on abstract comparison of different heat-generating media or comparison of unit prices of fuels is misleading. Each form of heat energy has its field of usefulness as well as its limitations, which vary with the nature of the heating process, plant conditions, geographic location, and many other factors, any one of which may decide the final choice.

It is also obvious that price alone cannot be made the basis of comparison between crude and highly refined fuels, because certain advantages such as continuity of supply, cleanliness, speed, safety, convenience of handling, and simplicity of operation must also be taken into consideration to make the comparison of real economic value.

Our specific case of heating oils and varnish ingredients is one which requires that the heating equipment be designed to meet the following conditions. Its rate of heat output per unit of time must be sufficient to produce and duplicate a predetermined temperature rise for a batch of given size; also, its turn down capacity must be low enough to maintain the materials at any desired holding temperature, for any duration of time, during the bodying period. Rate of heat input during the initial heating up period and uniformity of temperature during the holding period are closely associated with degree of bodying and final viscosity of the finished product.

The paint and varnish trade of today demands uniform viscosities for every batch, and it is no longer satisfied to blend several under- or overheated batches to produce apparent viscosities in that manner.

Since our problem deals with heat and its application, it is desirable to include a few statements concerning its behavior and characteristics. When a substance is heated, the absorption of heat is manifested by temperature rise which can be measured by instruments; this so-called "sensible heat" is expressed in degrees F. and is measured by thermometers or pyrometers. Some substances when heated not only show temperature increase, but also, at some definite temperature, pass through a physical change; that is, solids become liquids, and liquids change to vapors. The quantity of heat necessary to cause a change of state is called "latent heat" of either fusion or vaporization, according to the kind of physical change that takes place. Latent heat cannot be measured by thermometers and is expressed in number of heat units, Btu's, required to effect the change of state.

Various substances also have different capacities for heat absorption, so that equal heating effects will produce different temperature rises for each substance. This property, called "thermal capacity," is the basis of heat input and heating efficiency calculations. Quantitative measure of thermal capacity is specific heat, which multiplied by temperature rise and weight of charge gives the total heat content in Btu's. The term specific heat is the ratio of quantity of heat required to raise unit weight of given substance to that required to raise an equal weight of water, both one degree in temperature.

Another property that varies with the nature and the composition of materials is their ability to convey heat from point to point within their mass. It is called "thermal conductivity." This property is expressed in Btu's transmitted through given thickness and area of a substance per unit of time and is proportional to temperature gradient.

Oil and varnish heating processes also involve heats of chemical reactions. These reactions take place during the bodying and polymerization periods and are highly complex. It seems logical to assume that heat energy is necessary to build up large molecules, so that reactions of bodying and polymerization are for the major part endothermic. It also appears plausible that high temperatures cause a certain amount of thermal decomposition during which some of the large molecules break down and others are destroyed by oxidation. Consequently, thermal decomposition and oxidation reactions are exothermic. Since these various heat-absorbing and heat-producing reactions take place simultaneously, but at different rates, their quantitative values are difficult to determine; therefore, our present knowledge of their behaviors is very limited. We know, however, that they

take place at increasing rate at high temperatures and tend to become violent above certain critical temperatures.

The heat requirements of a typical oil or varnish batch consist of the following items:

1. Heat absorbed by batch ingredients.
2. Heat absorbed by kettle.
3. Heat absorbed by furnace setting.
4. Heat lost by radiation, convection, and conduction.
5. Heat carried off by flue gases, in case of fuel heating.

The quantity of heat absorbed by batch ingredients and by kettle is relatively simple to calculate provided sufficiently reliable data are available on specific heats of the materials involved.

Figures 1 to 5 taken from data by Long, Reynolds, and Napravnick (*Ind. Eng. Chem.*, **26**, 866 [1934]) and by Delaplace (*Compt. rend.*, **208**, 515 [1939]) give the specific heats of several frequently used bodying oils. It is interesting to note that curves for all the oils except linseed show gradual and uniform increase in specific heats with increase in temperature, whereas those for linseed oil show an inflection. W. H. Gardner and J. Mattiello have suggested that these S-shaped curves may be due to a tendency for linseed oil to change and polymerize at temperatures above the point of inflection. Long and his co-workers have pointed out that exothermic chemical reactions most likely take place at these temperatures. So, when estimating heat input of a liquid charge, we cannot take specific heat corresponding to either initial or final temperatures, but must estimate the average specific heat for the entire given heating range.

When dealing with solids we are confronted with serious lack of reliable data concerning their thermal constants. We know that when heating resins and other solid ingredients there exists a gradual and highly indefinite transition from solid to liquid state, which undoubtedly includes the sum total of specific heats plus latent heats of fusion, through the entire heating cycle. These solid bodies belong to the rather broad class of mixtures which have no distinct melting points and other specific properties associated with pure substances. In some respects these solids act as supercooled liquids which have no definite heats of fusion. Therefore, for the purpose of heat input calculations, the best we can do is to select some average value which for lack of better name may also be called "average specific heat."

Because of limited knowledge of this subject, the New York Paint and Varnish Production Club is now collecting information on the effects of heat on paint and varnish materials, which, when completed, will give us the much-needed answers to several heat problems.

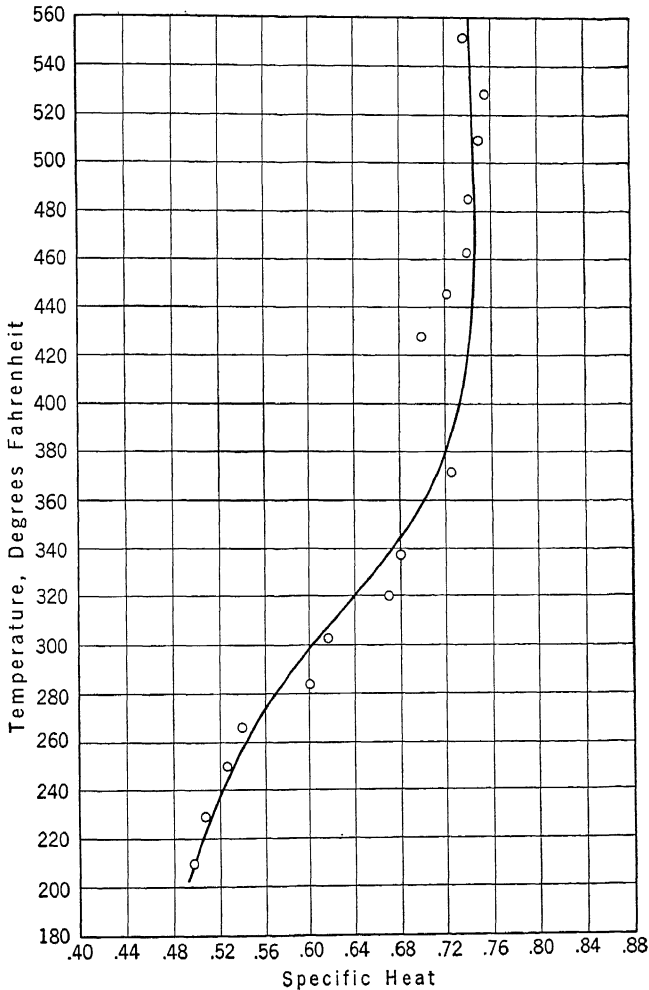


FIG. 1. Specific Heat of Raw Linseed Oil. I Value = 194 and Acid Value = 1.53.

To illustrate the method of calculation, we take an 800-pound batch of raw linseed oil to be heated from 60 to 550° F. in a copper kettle weighing 220 pounds.

	Weight in Lb.		Average Specific Heat		Temperature Rise		Heat Content in Btu's
Oil .....	800	×	0.58	×	490° F.	=	227,360
Kettle ....	220	×	0.104	×	490° F.	=	11,210
Heat absorbed by oil and kettle .....							<u>238,570</u>

A calculated heat input is of value only for estimating combustion equipment capacities and for determination of heating efficiencies.

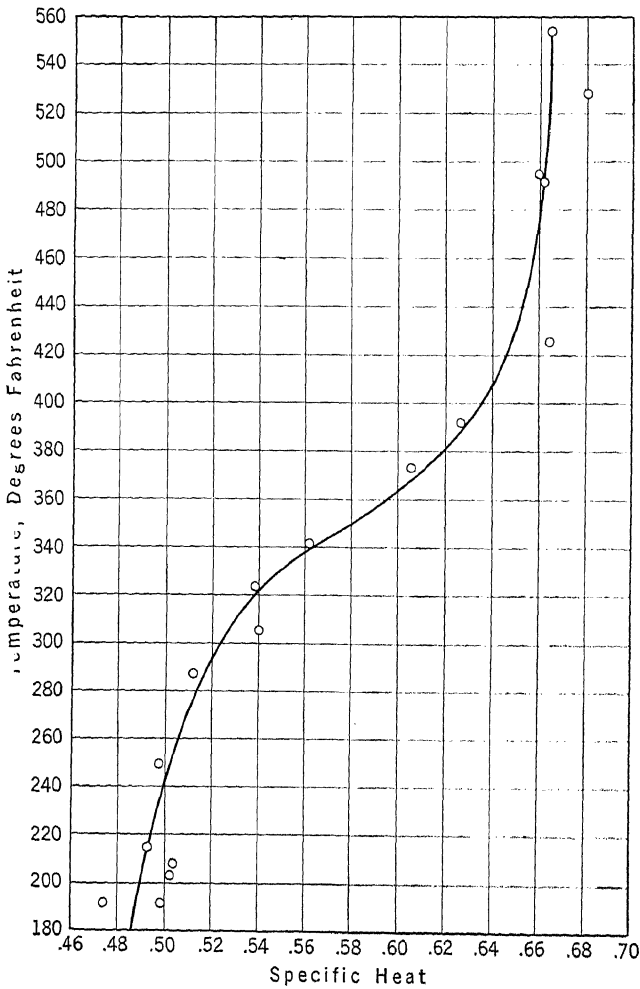


Fig. 2. Specific Heat of Linseed Oil, Alkali-Refined. I Value : 156.7 and Acid Value = 3.10.

It is important to remember that this quantity of heat units is purely theoretical and can never be met in practice. The overall efficiency of a varnish fire is largely dependent on furnace design,

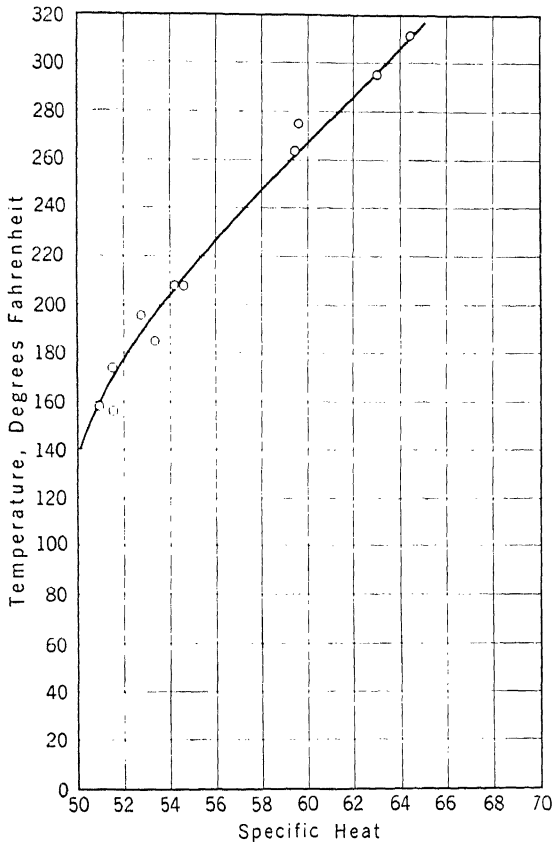


FIG. 3. Specific Heat of Tung Oil. I Value = 156.7 and Acid Value = 3.1.

nature of heat source, operating practice, etc. Because of their respective importance on thermal efficiency, these various factors are treated in more detail later on. The thermal efficiency of a given varnish fire may be expressed briefly by the following formula:

$$\frac{\text{Btu's absorbed by batch ingredients and kettle}}{\text{Btu's input of heat source}} \times 100 = \text{Per cent efficiency}$$

To calculate the additional heat requirements which were previously listed as heat absorbed by furnace setting, heat lost by radiation, con-

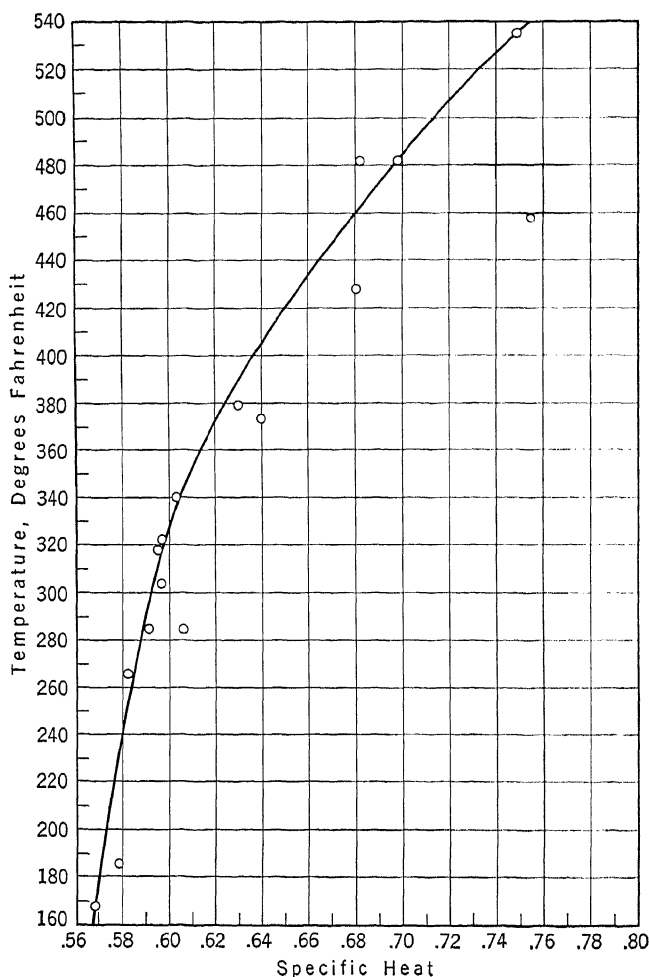


Fig. 4. Specific Heat of Soybean Oil. I Value = 134 and Acid Value = 2.3.

vection, and conduction, and heat carried off by flue gases requires rather involved engineering calculation which is beyond the scope of this chapter. Such calculation, which should be performed by an experienced heating specialist, is used as a basis of equipment design. For our purpose, the additional heat input to balance these items may

be briefly summarized under a convenient heading or "effective heating efficiency."

Just what is effective heating efficiency and how can it possibly be determined? How much of it is properly due to equipment design,

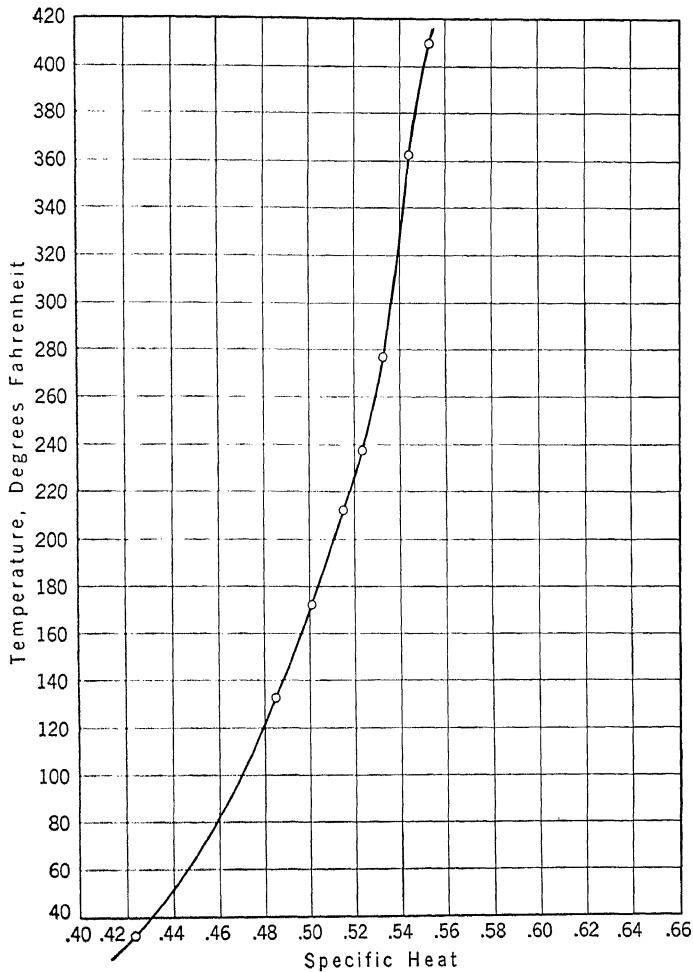


FIG. 5. Specific Heat of Castor Oil.

how much to choice of heat source, and how much should be charged to care or carelessness of operation. Perhaps these questions may be at least partially answered by detailed analysis of the contributing causes and their effects on heating efficiency.



Suppose we start with open fires and try to determine whether the furnace and kettles are designed for good heat transfer. We find that the average cooking room has a collection of kettles varying in shape, size, and materials of construction. Portable kettles range from 36 inches to 48 feet in diameter and depth, and from 180 to 375 gallons in capacity. Some are flat-bottomed, others dish-shaped. Some are made of copper, others of Monel, aluminum, or stainless steel. These materials of construction are chosen to meet the needs of a particular batch. So far as heat transfer efficiency is concerned, thermal conductivity of some particular metal is far less important than the size and shape of the kettle and its relative vertical position above the fire pit. The apparent advantage of better thermal conductivity of some metal as compared with others is very slight in proportion to resistance to heat flow caused by film of stagnant oil or varnish left over from previous batches. Clean kettle interior and continuous stirring go a long way toward improving heat transfer without depending too much on theoretical heat conductivity of some metal walls.

For convenient changing of kettles, open fires are recessed below ground level in close contact with earth, nature's own heat equalizer. So the first item to consider is dissipation of heat from fire pit into surrounding ground. Heat flows like water from higher to lower levels—of course, levels of temperature—and, like water, its flow can be obstructed or retarded by suitable means.

Best-known obstructors to heat flow are porous fireproof materials because their minute air pockets and tiny particles of solid matter offer tremendous resistance to passage of heat. Since heat is transmitted through solids from one particle to another by conduction, and through gases by convection and radiation, heat passage within a porous medium necessitates repeated change from radiation and convection across air spaces to conduction through solid particles. Now, if the air pockets are very minute and uniformly distributed, no appreciable convection currents can be set up, nor can radiant energy proceed across a barrier of a multitude of solid particles. Hence, whatever heat can get through is only by conduction in a roundabout way through slender points of contact between solid particles. When the porous medium is composed of material having low thermal conductivity, it becomes an excellent heat insulator and gives us effective means of stopping heat losses.

So now we may list insulation of fire pit as the first important cause contributing to heating efficiency.

In addition to adequate insulation which prevents loss of heat from fire pit, another precaution is necessary, that is to stop flow of moisture from the ground into the pit. Evaporation of moisture costs money, and full precautions should be taken to stop this wasteful loss of heat. Waterproofing of outer walls of fire pits is the obvious answer to this problem. Therefore, leakage of heat into the ground is a second variable affecting heating efficiency.

Heat absorption by materials of furnace construction is proportional to areas of surfaces exposed to heat flow, and the rate of heat absorption per given surface area is proportional to density and thermal conductivity of the materials. The quantity of heat stored in furnace walls depends on their temperature, which in turn is influenced by wall thickness, density, and specific heat of refractories used. In plain words, quantity of refractories should be limited to that necessary for strength and durability, and volume of fire pits should be restricted to combustion space required by given fuel.

Thick heavy fire brick walls store up large amounts of heat during the early stages of heating, and frequently it becomes difficult to maintain even temperatures during bodying periods. The old practice of pulling the kettles over the edge of the fire pit to stop the temperature from coasting is just a bad habit inherited from the "good old days" when fuel was cheap and heating methods crude. The modern way is to design fires for minimum heat storage and control the fuel input by instruments without juggling of kettles.

In the past few years the ceramic industries have developed new so-called insulating refractories, which have a very low heat storage capacity, low thermal conductivity, and good resistance to flame action. These new refractories are just made to order for fire pit construction with liquid or gaseous fuels. Their heat capacity is from 40 to 75 per cent less than standard fire brick so that temperature coasting due to heat storage need no longer be feared.

Being poor heat conductors, insulating refractories quickly attain high surface temperatures, making it possible to convert a high percentage of heat of combustion into radiant energy. When the refractory surfaces are shaped so that most of the radiant heat is directed toward the kettle, we obtain more effective heat transfer.

Radiant energy is very desirable for speed; however, its intensity drops very quickly with distance. In order to obtain maximum benefit from its energy, the heat source should be as close as possible to point of application; otherwise a large portion of radiant energy will be dissipated into atmosphere.

Hence, choice of materials of construction and design of fire pit are other causes of effectiveness of heating efficiency.

Inside dimensions of fire pits depend on required maximum heat input, and on choice of fuel as well as its combustion characteristics. As a general rule, volume of combustion space, for equal Btu output, diminishes with increase in refinement of the fuel. Solid fuels require fire pits of greater depth and larger surface area than liquid fuels; heavy oils need larger combustion space than light oils; and gaseous fuels can be completely burned in far less space than solid or liquid combustibles. Hence, the furnace setting should be designed to suit one fuel only, and, in case of change from one fuel to another, the furnace should be completely redesigned. The relations between fuels and furnaces are important and have definite influence on heating efficiency.

In connection with fuel choice, heat distribution under kettle is of prime importance. If any external point of kettle surface is heated at a faster rate than heat can be absorbed by charge in the kettle, the metal soon becomes overheated and the life of the kettle is shortened.

Another item to consider is uniform rate of heat absorption by batch ingredients. Rate of bodying is proportional to temperature so that, when some portion of the charge absorbs heat faster than other portions, the oils build up viscosity faster in hot zones and more slowly in cooler zones. When heat distribution under kettle is not uniform, the finished batch is likely to consist of a heterogeneous mixture of over- and underpolymerized particles.

Local spot heating may, of course, be avoided by constant stirring of the batch, which, if done by the operator, requires that he be properly protected from heat. This point brings us to the last important item of effective heat utilization, which is closely associated with cooking room comfort. The problem is to utilize as much available heat as possible in flue gases rising from the fire pit and to restrict their flow to useful kettle heating.

The heating efficiency of an average underfired kettle, when fully exposed to drafts and without proper shields to direct hot flue gases against its sides, is highly variable. Poorly designed open fires, regardless of kind of fuel used, may have effective heat transfer efficiencies as low as 5 per cent, and the best that can be obtained on open fires of modern design, however, without shielding, is about 35 per cent. Now, if proper precautions are taken to utilize the other-

wise wasted heat in flue gases, the efficiencies rise to as much as 60 per cent, or even better.

The problem of shielding movable kettles is rather difficult. The customary curved metal shields are good heat conductors and radiate heat toward the operator as much as an exposed kettle; also removal of hot shields at completion of batch requires special handling for protection from burns. Because of heat action and frequent handling, movable heat shields have a very short life and are soon discarded as a nuisance.

A better way to increase heating efficiency of movable varnish kettles, as well as to provide cooking room comfort, is to utilize flue-connected permanently inclosed settings and to move kettles by overhead trolleys in and out from settings to cooking and thinning rooms. The overhead trolley or conveyor system is far superior for ease of kettle handling, and there is no hot truck chassis in the operator's way during cooking. A closed fire pit directs hot flue gases toward the sides of the kettle for better heat transfer efficiency, and an independent flue removes the gases from the operator's proximity for safety and comfort.

Since bodying of oils is generally done on much larger scales than varnish processing, the kettles are invariably inclosed in permanent settings; the design of furnace structure depends on choice of heat source. With gas fuel it is desirable to avoid all brick work because gas burners need no elaborate combustion chambers. Either a simple double wall metal jacket filled with rockwool or an insulating refractory setting inclosed in sheet metal is satisfactory. With liquid fuels a properly proportioned firebrick combustion chamber is essential while the superstructure may be of similar design as for gas. Modern settings for electric, gas, and oil heating are shown with discussions of heating characteristics of these heat sources.

### **Solid Fuels**

Wood, coal, and coke were the pioneer solid fuels for industrial heating, used long before oil and gas began to appear on the market. The solid fuel-fired oil and varnish pits are so well known that a description of them would be superfluous. Even at the present time coal and coke fires still outnumber the so-called modern fuels by a generous margin.

Although coal and coke have an apparent advantage of low cost of heat units per pound of fuel, when all other costs, such as value of storage space, handling, ash removal, time consumed in starting of

fires are considered, the final heating cost often comes very close or even exceeds that of oil or gas. Coke when available at equal price is generally preferred to coal because of lower ash content and smokeless combustion.

Hand-fired solid fuels are not suited for the processing of small batches of high-grade materials when prescribed temperature gradient must be followed. However, a fair measure of temperature control can be obtained by installation of an automatic stoker with a forced draft system which permits close regulation of rates of fuel input and speed of combustion. The mechanical feed and forced draft system can be adjusted to give good heating performance without moving the kettles to the edge of the fire pit, and it is far superior to hand fires.

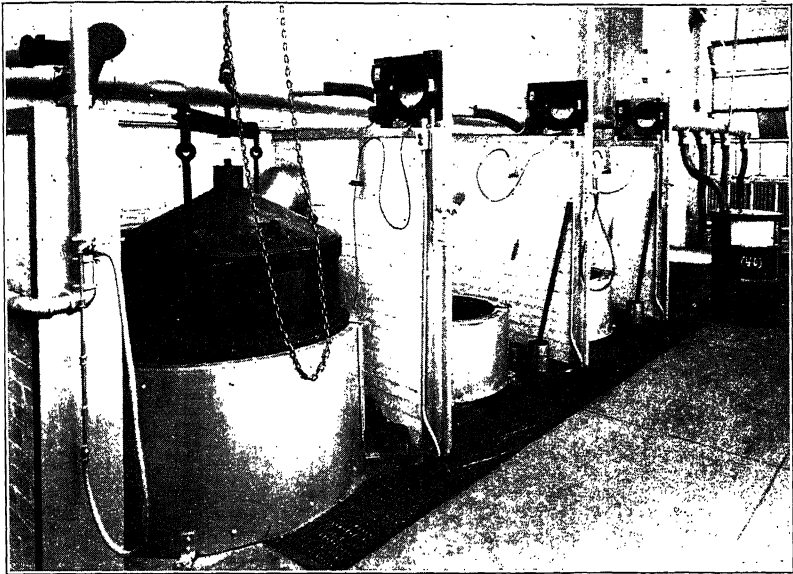
When tended to by an experienced fireman, a solid fuel fire gives good combustion efficiency which will be proportional to the amount of care it receives. To maintain uniform temperature distribution under the kettle hand-fired fuels require frequent trimming. The actual temperature of the hot gases rising from the fuel bed is very seldom uniform, and is likely to vary from one extreme to another across the surface area of the bed. Such variations are caused by stratified air flow through either porous or compacted layers of ashes or fuel which accelerate or retard combustion. To repeat, a coal or coke fire is as efficient as the operator's willingness, skill, and degree of attention make it.

### Gas Fuels

There are three commercially available gas fuels: manufactured gas, natural gas, and liquefied petroleum gases. The first two are supplied through public utility service lines, and the last is delivered in tanks for storage on the user's premises. Gases are clean, concentrated, pure fuels, free from residues and having fixed heating values. Those delivered through utility pipe lines are ready for use without additional preparation and are available in such quantities as may be required without storage.

Combustion of gases is very simple; both the fuel gas and the air are freely miscible so it is easy to produce, as well as duplicate, combustible mixtures for any desired flame. When required, the air-gas ratio may be set for exactly the theoretical mixture which can be burned under closed settings without additional air. Sealed-in gas burners installed in fireproof heating chambers are excellent means of fire protection in case of spillage or boiling over of the hot batch.

The most important properties of gases, as applied to heat generation, are their low density and compressibility. Gases can be conveyed through supply lines with low-pressure drop and discharged through a small orifice without danger of stoppage. Combustible gas mixtures always expand to the full volume of the burner body so that every burner port delivers flames corresponding to its full area



*Courtesy of Kientle and Co.*

FIG. 6. Illustrating Gas Heating for Bodying Drying Oils and Varnish Making in Semi-enclosed Kettles.

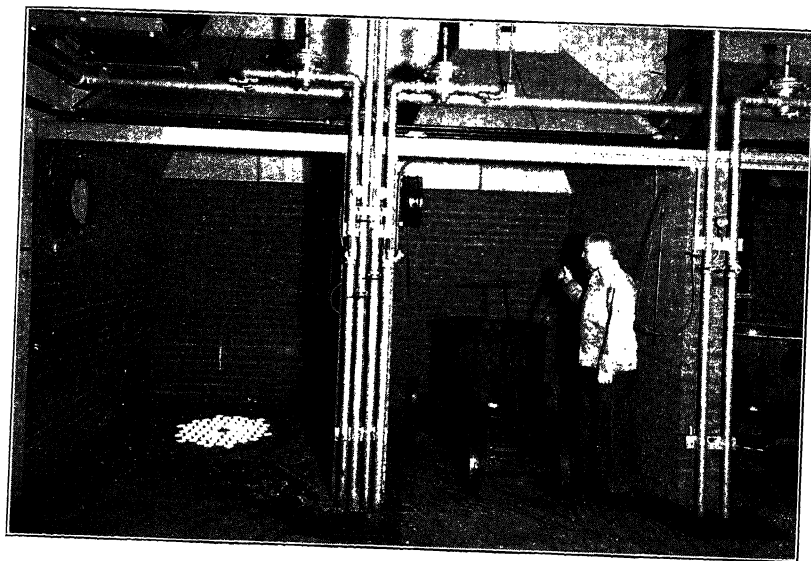
and the static pressure of the combustion system. Since the delivery pressure may be varied over a considerable range within limits of speed of flame propagation, the heat output per flame may be varied accordingly. These facts, briefly stated, account for the wide range of flexibility of gas burners.

As compared with solid and liquid fuels, combustion space requirements for gases are almost negligible. The actual combustion space, i.e., volume occupied by flame, depends on initial air-gas concentration. As this ratio approaches the theoretical mixture, speed of combustion increases until visible flame almost disappears. Large heat output, therefore, may be confined, if desired, within narrow or shallow heating spaces.



*Courtesy of National Lead Co.*

FIG. 7. Illustrating Gas Heating for Bodying Drying Oils and Varnish Making in Fully Enclosed Kettles.



*Courtesy of Selas Co.*

FIG. 8. Illustrating Gas Heating for Bodying Drying Oils and Varnish Making over Open Fires.

Because of the unique combustion properties of gases, it is possible to subdivide the total estimated heat input between a number of small burners and locate each burner on the most advantageous position for uniform heat distribution. Single-flame or multiport burners can be manifolded in groups to separate controls so that even a small sample batch can be processed under prescribed full batch conditions by selective operation of the control system.

Since each gas burner is a complete miniature combustion unit, separate combustion chambers or fire pits are not needed; consequently no heat is stored in refractories and dissipated at the end of the run. The absence of stored heat in modern gas-fired settings permits close temperature regulation with minimum of attention.

Selection of gas combustion system and burner equipment should be based on total number of kettles and other gas uses in the plant. For example, gas at the city main pressure, with air at one pound, may be delivered to suitable burners through automatic proportioning mixers to several adjacent cooking kettles. A more elaborate combustion system may be advantageous in a plant where, in addition to oil and varnish processing, inert gases are produced, by combustion, for air displacement in storage tanks. The majority of gas utilities maintain a specialized heating service which should be consulted for correct recommendations of equipment best suited for specific uses.

### Liquid Fuels

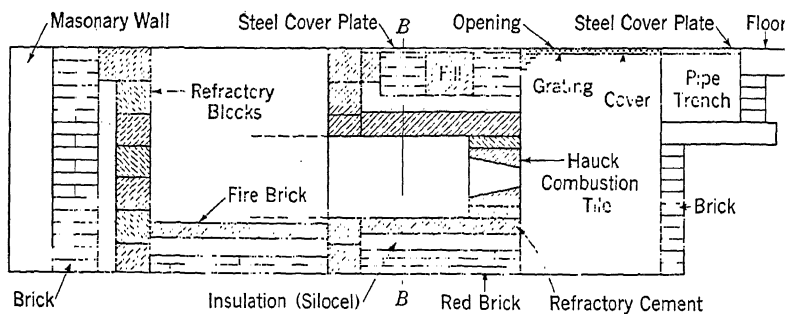
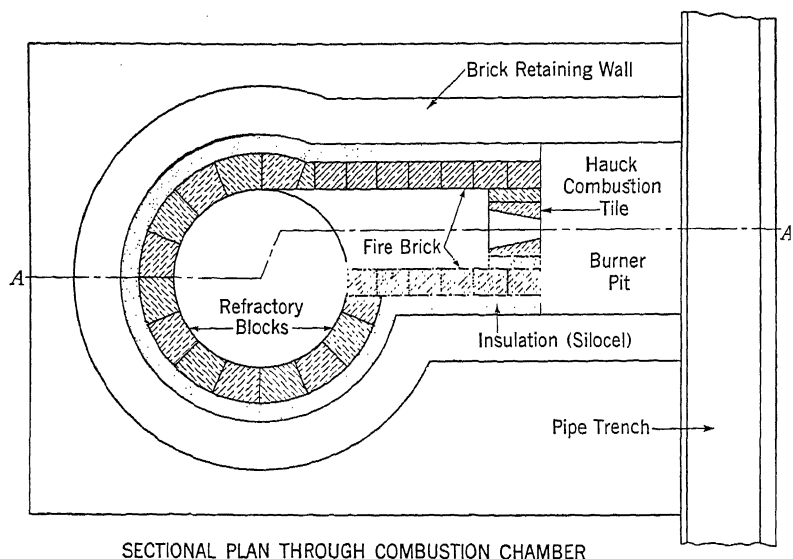
Combustible oils do not burn in a liquid state. To start combustion the oils must first be vaporized, the vapors intimately mixed with air, and the vapor-air mixture raised to its particular ignition temperature. This is in accordance with well-known relations between temperature and physical state of liquids. Since ignition temperature of any oil vapor is in all cases much higher than the boiling point and vaporization temperature of the liquid, it becomes easy to understand why oils do not burn in liquid form.

During the combustion process liquid fuels first pass through the preliminary stage of vapor formation and then through a series of successive hydroxylation and thermal decomposition reactions. These various physical and chemical changes require a certain amount of time and space. For these reasons an oil fire requires larger combustion volume and longer room for flame travel than gaseous fuels.

The design of an efficient oil-burning fire pit is no longer a job for a bricklayer but an engineering problem for a specialist in that field. The furnace setting for oil firing depends on the type and the fuel



capacity of a given oil burner. Size and shape of combustion space require careful design to prevent spot heating of the kettle or injury to refractories by flame action. Since uniform heat delivery to the



*Courtesy of Hauck Manufacturing Co.*

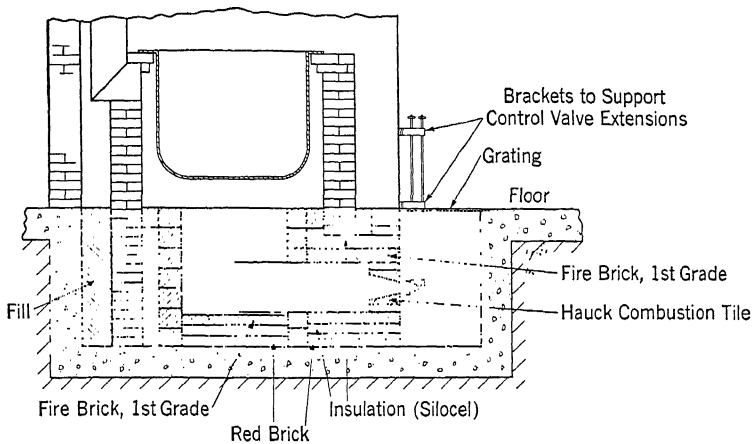
FIG. 9. Hauck Rotating Flame Type Varnish Fire Setting.

kettle is of prime importance, the shape and dimensions of the furnace should correspond to kettle size as well as oil burner characteristics.

The present tendency is tangential or rotating flame type settings in preference to center firing. The circular motion of hot gases in-

creases flame travel, prevents direct flame impingement, and is therefore less destructive to refractories. Some manufacturers favor a refractory pedestal in the center of the fire pit to insure maximum of circular gas motion, and they leave the top of the fire pit open; others recommend perforated diffusion domes as added protection against flame impingement. Either arrangement is intended to prevent flame contact with the kettle bottom and to produce uniform heat distribution.

The function of an oil burner is to atomize the oil thoroughly so that it will vaporize quickly and completely and also to mix the vapors



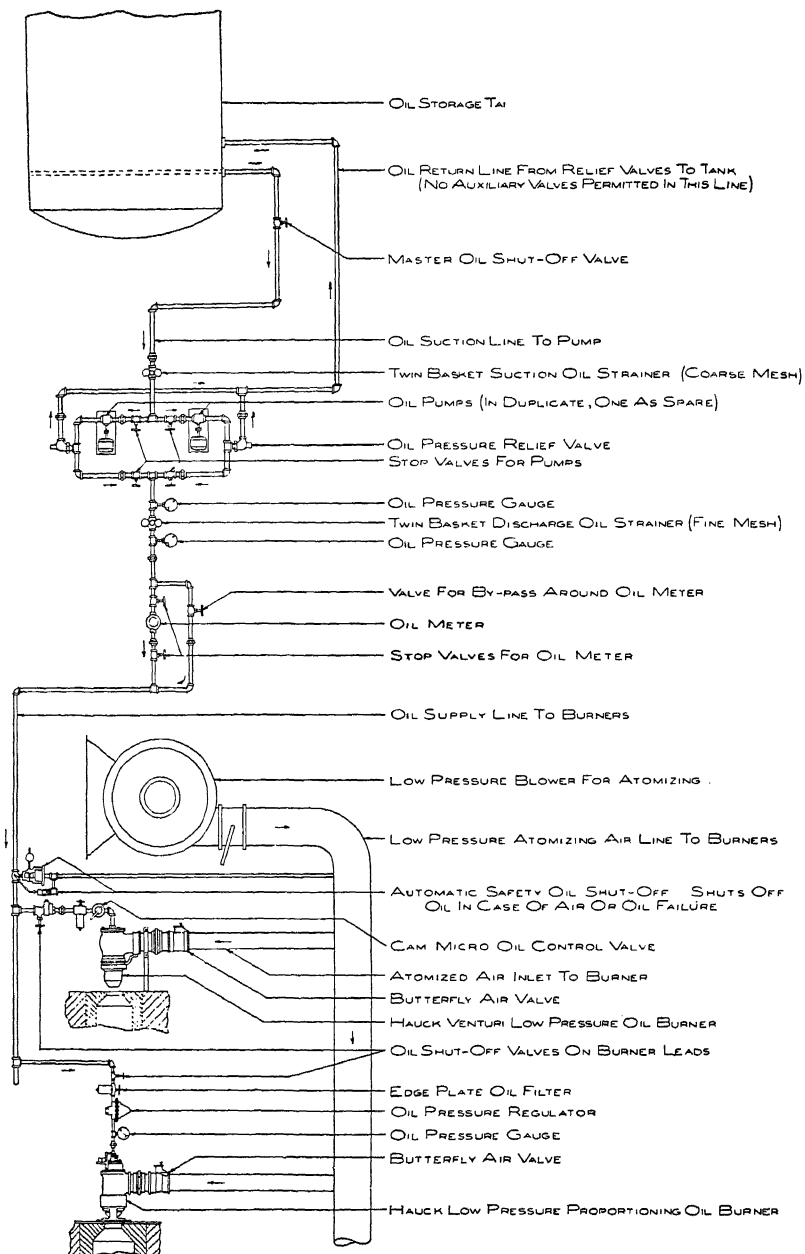
*Courtesy of Hauck Manufacturing Co.*

FIG. 10. Firing Setting for Stationary Type Varnish Kettle.

with a proper amount of air for efficient combustion. The fuel-air mixture is ignited and maintained well above its ignition temperature in a refractory combustion tile or tunnel which also serves to stabilize the flame, i.e., keep it from blowing away at high combustion rates.

Selection of an oil burner should be made mainly on the basis of flexibility, i.e., range of fuel-burning capacity between maximum and minimum plus ease of operation and control. Turn down range is very important for duplication of cooking cycles on different-sized batches. Automatic proportioning of primary and secondary atomizing air and quantity of oil at all ranges of turn down are very desirable for fuel economy and simplicity of operation.

The following drawings of rotating flame type varnish fire settings represent a typical well-designed insulated oil-fired pit for movable



*Courtesy of Hauck Manufacturing Co.*

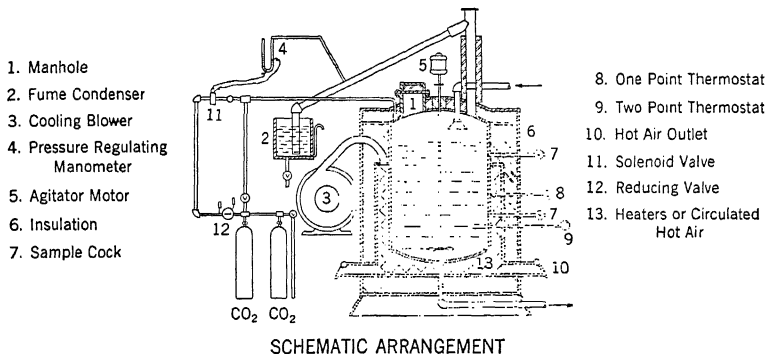
FIG. 11. Typical Layout of Auxiliary Oil-Burning Equipment.

kettles and a modification of the same setting for stationary partially enclosed oil-bodying kettle.

The handling and combustion of fuel oils require the following apparatus: an oil storage tank of ample capacity to insure continuous fuel supply in case of interruptions in delivery; two high-grade oil pumps, interconnected so that either is instantly available for service when needed; a system of oil strainers for removing deposits and accidentally entrained solids; an air blower or compressor of suitable capacity and pressure characteristics to suit burner design.

### Heating by Electricity

Utilization of electric energy for processing of oils and varnish has the advantage of complete absence of products of combustion, which greatly simplifies ventilation so far as the heat source is concerned.



SCHEMATIC ARRANGEMENT

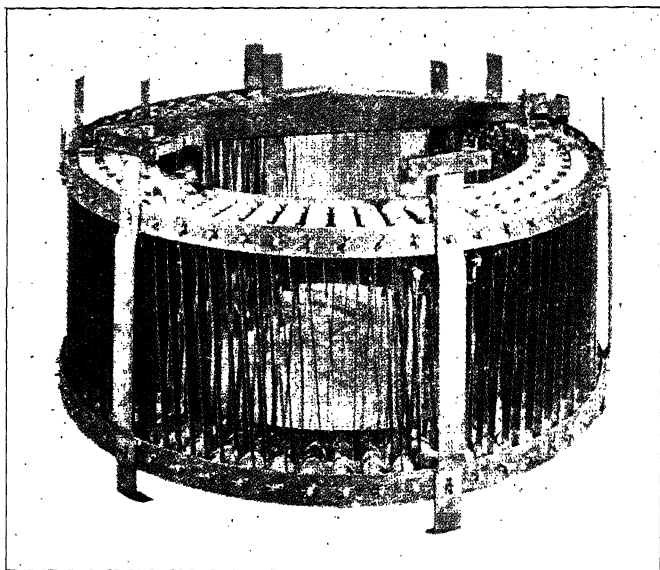
*Courtesy of Drever Co.*

FIG. 12. Bodying of Oils in a Closed System.

Electric heaters can be fully inclosed and placed in any desired position for uniform and efficient heat delivery to the kettles. However, in cooking rooms the major ventilation problem is disposal of fumes, which even with electric heat is no different from disposal when fuels are used. Electric heat is pure energy in most concentrated form, and consequently its Btu cost is relatively high; its use can be justified only in fully insulated, completely inclosed kettles and then only under favorable power rates. There are three distinctly different methods by which electric heat can be applied to processing of oils and varnish, namely, by immersion heaters, by external heaters, and by container resistance.

The immersion heater method gives the highest heat transfer efficiency and can be conveniently applied to bodying of oils, especially

when auxiliary cooling is also provided to take care of exothermic reaction. For best results constant mechanical agitation of the oil should be provided to prevent excessive temperature rise on the heaters and carbonization of oil on the heater sheath. When mechanical agitation is not used, heaters of much lower watt density should be installed so that the liquid is not locally overheated.



*Courtesy of Dreyer Co.*

Fig. 13. 125-Kw. Electric Immersion Unit for Linseed Oil.

It is very important to keep immersion heaters free from deposits of oxidized oil films, which if allowed to accumulate would carbonize and discolor the product. Since immersion heater coils are at best difficult to clean, the film formation may be easily avoided by immediate refilling of the kettle with a fresh charge of raw oil after completion of previous batch.

To save energy the external kettle surface should be insulated to stop dissipation of heat into the surrounding air. For this purpose, any block insulation suitable for 700° F. hot face temperature may be applied in most economical thickness as recommended by manufacturer.

The external heating method consists of sectional air heaters which are mounted in an air space between the external kettle surface and the outer insulated housing. Correct application of external electric

heaters calls for specialized engineering technique. The relative location of individual heaters and correct distribution of energy input per heater are important for efficient heat absorption by the kettle. Also the details of mounting for ease of replacement and group wiring for temperature control operation require careful design to make the installation easy to maintain and operate.

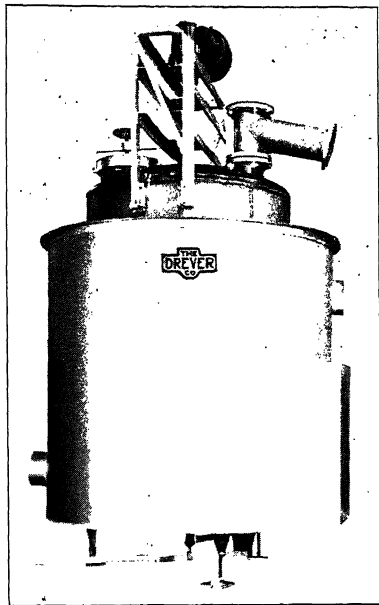
The main advantages of external heating are freedom from obstructions to oil motion inside the kettle and no extra oil-coated surfaces to clean. Another distinct advantage is the air space around the kettle which is valuable for natural or forced convection heat equalization and for even more important forced cold air circulation cooling. These advantages are more than sufficient to offset the lower heat transfer efficiency of external heaters as compared with immersion heaters.

The container resistance method utilizes walls of the oil-filled vessel as the heat source; electric current of suitable watt density is passed through container walls and resistance of the metal to flow of current generates heat which is absorbed by the oil.

This method is applied by one manufacturer by utilizing a series of nickel chrome steel tubes the walls of which are heated through their own resistance to electric current. Oil is circulated through the hot tubes by pumps, under close temperature control, and when raised to bodying temperature is transferred to well-insulated storage tanks and held there for some specified time to attain desired body. In this manner one heater can supply an entire plant with hot oil and so displace several movable kettles.

### Heat Transfer by Fluids

The heat transfer by fluids has a distinct advantage in that a single heat generator can be used for simultaneous processing of several



*Courtesy of Dreyer Co.*

FIG. 14. 500-Gal. Working Capacity Electric Processing Kettle.

batches of material, and each is processed independently at its own particular time and temperature cycle.

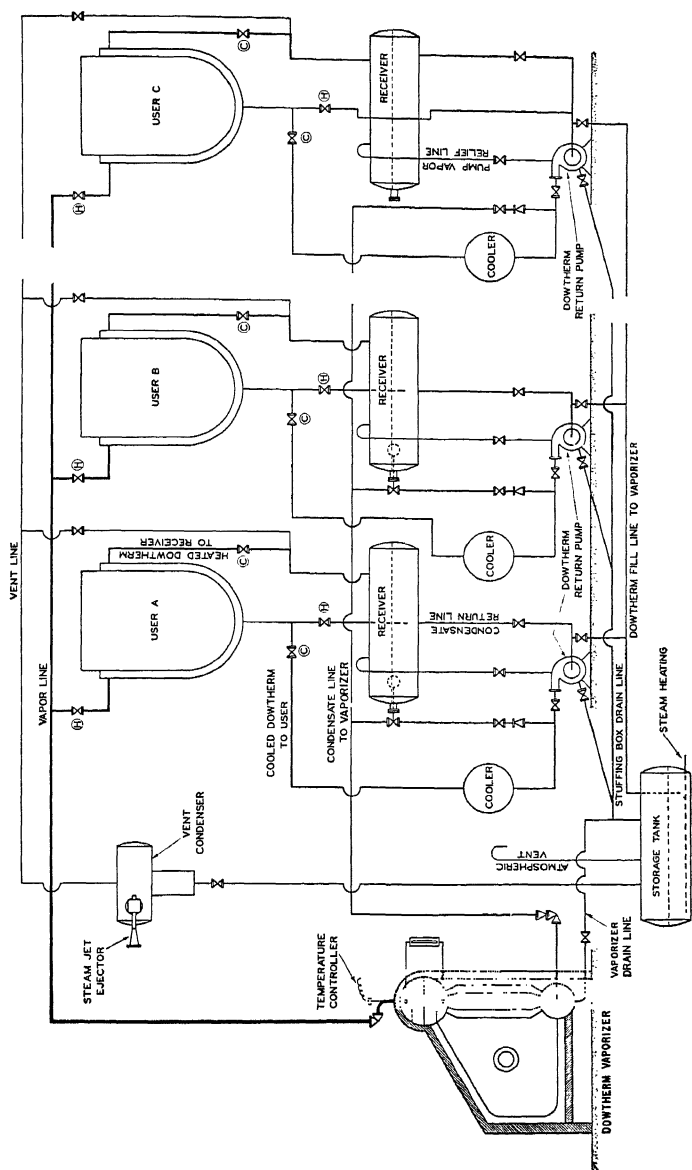
The ideal fluid for heat transfer processes is steam. However, its practical temperature range is not high enough for processing of oils and varnishes because, to meet the required temperatures, very high steam pressures would have to be used. Because of the demand for some satisfactory heat transfer medium for higher processing temperatures, considerable time and effort were devoted to this problem by various heating specialists and many substances were tried with varying degree of success. Heat transfer by circulation of hot air, of hot flue gases, and hot oils, although excellent for many applications, depends on the difference between inlet and outlet temperatures of the moving fluid. Gases and oils have low specific heats so that large quantities of these fluids at high temperature differentials must be circulated to accomplish desired heating effects.

A heat transfer fluid which reaches the point of application in the form of vapor, and returns to the heat source as liquid, is very desirable as its heat of vaporization is liberated at point of condensation. In this manner greater heating effect is obtained per unit weight of heat transfer medium than can be obtained by non-condensing fluids.

The desire to find a liquid-vapor phase fluid that would be suitable for temperature above the practical range of high-pressure steam led to the development of a new high temperature heat transfer medium called Dowtherm A. This compound has all the desirable properties of steam plus the advantages of a high boiling point and low vapor pressures at elevated temperatures. Dowtherm A is an eutectic mixture of 26.5 per cent diphenyl  $(C_6H_5)_2$  and 73.5 per cent diphenyl oxide  $(C_6H_5)_2O$ . The mixture melts at  $54^\circ F.$  and the liquid boils at  $500^\circ$  at atmospheric pressure. Specific heat of the liquid is 0.63, and latent heat of vaporization is 123 Btu per pound at boiling point.

Since the physical properties of Dowtherm are radically different from those of steam, the Dowtherm heating systems require special design of boilers and heating surface capacities. The greatest advantage of Dowtherm over steam is due to its characteristic low vapor pressure which permits its use for high heating temperatures at relatively low operating pressures. Dowtherm has a pleasant geranium-like odor, and both the liquid and vapor are non-toxic and non-corrosive.

The accompanying diagram (Fig. 15) illustrates a Dowtherm vaporizer serving several users, each of which may be independently con-



*Courtesy of Foster Wheeler Corp.*

Fig. 15. "Dowtherm" Heating System for Bodying Drying Oil and Varnish Making.



trolled by throttling the admission of Dowtherm vapor to the heating section. A separate cooking circuit is also provided by means of which liquid Dowtherm, passing through the cooler, is continuously cooled by water and may be used to reduce the temperatures of the products within the kettles at the ends of the heating periods. The provision for cooling together with heating may also be used to control the rate of heating of products which themselves generate heat after being raised to certain critical temperatures.

Each of the users as shown has a two-section heating jacket arranged so that the bottom section or both sections may be operated as desired. During the heating cycle, valves marked *H* are open and valves marked *C* are closed, and the return pump for any user is in full operation. Dowtherm vapor entering the user will be condensed and will be returned to the vaporizer as rapidly as the condensation enters the pump. Valve *H* may be throttled to any extent desired to reduce the temperature of the vapors entering the user and to control operations independently of the requirements of any other user. The return pump is of the centrifugal type and operates continuously without control. A small recirculation line connected to the discharge of the pump provides for the release of vapors which might be generated within the pump to avoid vapor binding. At the end of the heating, valves *H* are closed and valves *C* are opened and circulation may be started through the cooling circuit. Liquid Dowtherm within the receiver is then forced to fill the circuit and will cool the product at a predetermined rate.

It is customary to provide the system with a storage tank capable of holding a full charge of Dowtherm for the system including the vaporizer. Such a storage tank should be fitted with a steam coil to protect the Dowtherm against freezing during periods of extremely cold weather.

A vent condenser with an ejector is a useful accessory which permits the evacuation of non-condensibles from the system either before or during operation and provides for return to the system of such Dowtherm vapor as may be carried with the non-condensibles.

According to data published by heating engineers specializing in Dowtherm applications, this fluid can be used for any processing temperature within the entire range of the paint and varnish industry, and there are now several successful installations in operation. So far no test data are available for publication purposes.

## Performance Data

Fuels will burn with 100 per cent combustion efficiency when a sufficient quantity of air is available to support combustion, provided the air is intimately mixed with the fuel gases or vapors and the combustible mixture is maintained above its particular ignition temperature during the entire combustion period. Shortage of air lowers combustion efficiency because the fuel does not become fully oxidized, and excess of air, while it still may produce perfect combustion, lowers temperature of the hot gases by unnecessary dilution and so retards heat transfer.

In fairness to all fuels, heat generation and heat transfer should be considered as distinct and separate functions. Fuel, burner equipment, and combustion chamber design influence only efficiency of heat generation, whereas efficiency of heat transfer to a charge in the kettle depends on method of kettle mounting, amount of heat-absorbing surface, means of directing hot gases toward kettle walls, degree of shielding from external drafts, stack pull, and many other variables typical of each installation.

The fuel consumption figures frequently given in trade publications quite often represent competitive data between run-down obsolete equipment and some just installed modern heat source and naturally show lower heating costs in favor of the new installation. In other cases, comparative heating performance is given in such vague terms as pounds, gallons, or cubic feet of fuel per 100 gallons of oil or varnish, with no mention of the nature of processed materials and time and temperatures involved. That kind of performance data is of no value except for commercial propaganda purposes.

To evaluate the performance of any type of heating equipment, accurate records of fuel consumption and production together with heating cycle data should be collected over a period of time in order to determine its behavior under various production conditions. In this manner individual variations due to human element and weather conditions are averaged and the equipment is given a chance to show true value in speed of heating, turn down range for holding periods, ease of operation and control, excess heat storage, and effects on cooking room comfort, which generally do not show up on so-called individual performance tests.

When accurate comparison of relative efficiencies of two furnace settings using the same fuel or new settings using other heat source

are desired, such tests, also of longer duration, must be conducted under similar time-temperature cycles with materials of equal composition and weight. To simplify calculations it is preferable to take straight linseed oil and determine the quantity of fuel expressed in Btu's required to raise a fixed weight of oil to some definite temperature, and determine heat consumption for entire holding period as a separate part of the test.

Because of the great many variables incidental to batch composition and processing practice, the following fuel consumption data are given to serve as an approximate guide of what may be expected from various heat sources, depending on their design, physical condition, and operating practice.

*Basis:* 100 gallons of oil or varnish as processed.

(1) Data on open fires with movable kettles:

Heat source	Heating system	Fuel consumption	Thermal efficiency
Coke	Hand-fired	120 to 180 lb.	7 to 12%
Coke	Forced draft stoker	90 to 110 lb.	15 to 19%
No. 4 oil	Low pressure atomization	6.5 to 12 gal.	11 to 24%
Manufactured gas	Multiport burners	1,200 to 1,600 cu. ft.	22 to 33%
	Radiant burners	1,100 to 1,500 cu. ft.	23 to 35%

The consumption of natural and mixed gases is proportional to equal Btu input for equal performance.

(2) Data on insulated closed settings with stationary kettles:

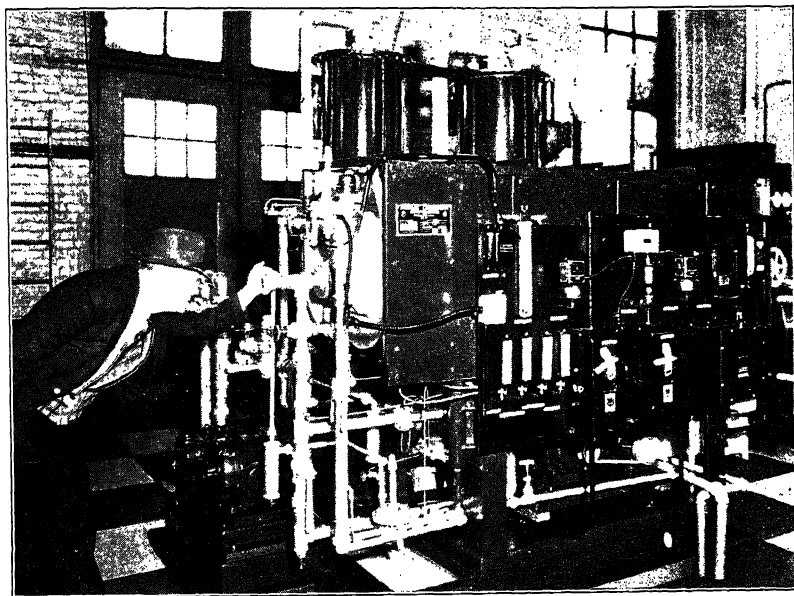
No. 3 or No. 4 oil	Automatic air-oil proportioning	3.0 to 4.5 gal.	35 to 50%
Manufactured gas	Immersion heaters	700 to 900 cu. ft.	52 to 57%
	Radiant burners	700 to 850 cu. ft.	50 to 66%
Electricity	Immersion heaters	70 to 78 kwhr.	84 to 92%
	External heaters	75 to 88 kwhr.	75 to 85%

## Protective Atmospheres

In addition to process heating there is another important fuel application which uses combustion methods to generate inert gases for protective blanketing of paint and varnish products from oxidation by air. Special gas atmospheres were originally developed for protection of metals from scaling and discoloration in furnaces during heat treating. They have been recently adopted to furnish protective atmospheres in chemical industries.

The paint and varnish field finds extensive application of inert gases for displacement of air in storage tanks and for blowing of syn-

thetic resins during cooking; inerts are also being tried for filling space above the surface of oxidizable products in cans for shipment, and are piped throughout plants for fire protection purposes. Blanketing of storage tanks with oxygen-free atmospheres eliminates the formation of skins and deposits over the surface of paint and on tank walls. The inert atmospheres help to reduce labor costs for frequent tank



*Courtesy of Surface Combustion Co.*

FIG. 16. Inert Gas Generator.

cleaning and replacement of filter screens. For blowing of ester gums, inert gases are far more economical than dry ice or bottled carbon dioxide and have no effect on the quality of the product.

The inert gas generator consists of an automatic proportional mixing device which continuously supplies a fuel gas-air mixture into a reaction chamber where the combustibles burn to produce an inert non-oxidizing mixture of water vapor, nitrogen, and carbon dioxide.

The raw inert gas is then passed through auxiliary cooling and scrubbing apparatus to condense the water vapor and remove all undesirable oxides of nitrogen and sulfur compounds. The generating equipment is always provided with suitable safety devices and automatic pressure-regulating governors, and is so designed that the entire

system is entirely automatic in operation to provide fixed composition inert gas in proportion to demand.

Although the use of inert gases is comparatively new to the paint and varnish industry, the material and labor savings obtained on several installations are reported as very favorable.

### Temperature Controls

The purpose of heat processing of oils and gums is to accomplish certain physical and chemical changes which impart new desirable properties that increase the usefulness and life of the processed materials. Since the degree to which the new properties may be developed depends on definite time and temperature cycle, an accurate temperature regulation during the entire heating process is of utmost importance.

The use of automatic temperature control equipment is very desirable because it regulates heat input in proportion to demand, thereby saving fuel or power; it guards the product from overheating and so prevents spoilage and minimizes fire hazard; it permits exact duplication of heat-processing conditions of each batch and thus assures uniform quality of product; it relieves the operator from constant watching of temperatures and heat sources; all this means better shipping schedules of quality products and increased profits.

In order to be able to regulate and hold temperature by instruments the heating equipment must have sufficient flexibility to do so by manual control. An instrument can do no more than the human hand, and, when properly taken care of, it will do its duty without forgetting. A temperature controller is actuated by a liquid-filled expansion element or by a thermocouple submerged in the contents of the kettle.

There are two general types of temperature controls: the throttling type, which provides incremental changes in heat flow proportional to changes in demand, and the "two-position" type, which starts and stops the entire heat source and so maintains temperature between two given thermometer settings. The throttling controls give closer temperature regulation than the two-position type. For close temperature regulation it is important that the heat source does not store excess heat in furnace setting as such energy would be released during the "off" period and cause the batch temperature to rise above the desired control point.

In addition to a suitable temperature controller, a so-called limit control is very valuable. Limit control may be a separate instru-

ment or simply an extra contact point within the controller circuit, which is set a few degrees higher than the upper limit of holding temperature. Its function is to take care of temperature rise due to exothermic reactions. A limit control may be wired to perform several things: to completely shut off the heat source, and then to start the flow of some cooling medium such as air, water, or chill back oil, or it may ring a bell and show a red light to call the operator's attention to the critical condition of the particular kettle. When the excess temperature condition is corrected the limit control may either be manually reset or be caused automatically to return to normal inactive position.

Successful application of temperature controls is closely related to method of heating, temperature requirements, and operating practice. For these reasons no specific control types are mentioned, as instrument manufacturers are best qualified to prepare correct recommendations to fit individual needs.

### **Fume Disposal**

During the cooking of oil and varnishes some constituents of the batch volatilize from the kettle in the form of fumes. These fumes possess characteristic penetrating and disagreeable odors so that their presence in the surrounding atmosphere is easily noticed, frequently causing complaints.

The fumes consist of: (1) low-temperature melting constituents of natural gums and rosin which are purposely driven off by heat for process reasons; (2) thermal decomposition and oxidation products volatilized from oils during bodying; and (3) volatile thinners which distill off during thinning of hot varnish.

The chemical composition of fumes varies with cooking formulas and heating cycle. The major constituents are largely higher fatty acids and aldehydes, mixed with variable proportions of water vapor, glycerol, acrolein, acetic acid, formic acid, and highly complex residues of thermal decomposition.

According to investigation of rates of fume evolution specially conducted for this book by Eberly and Mattiello, the average oil or varnish batch starts to give off fumes around 350° F.; the rate of fuming rises with temperature increase and reaches its maximum at about the time or shortly after the highest processing temperature is reached. After that, the rate of fuming slowly decreases, but never stops so long as heating is continued. The initial fume formation is largely due to loss of moisture and volatile constituents which are

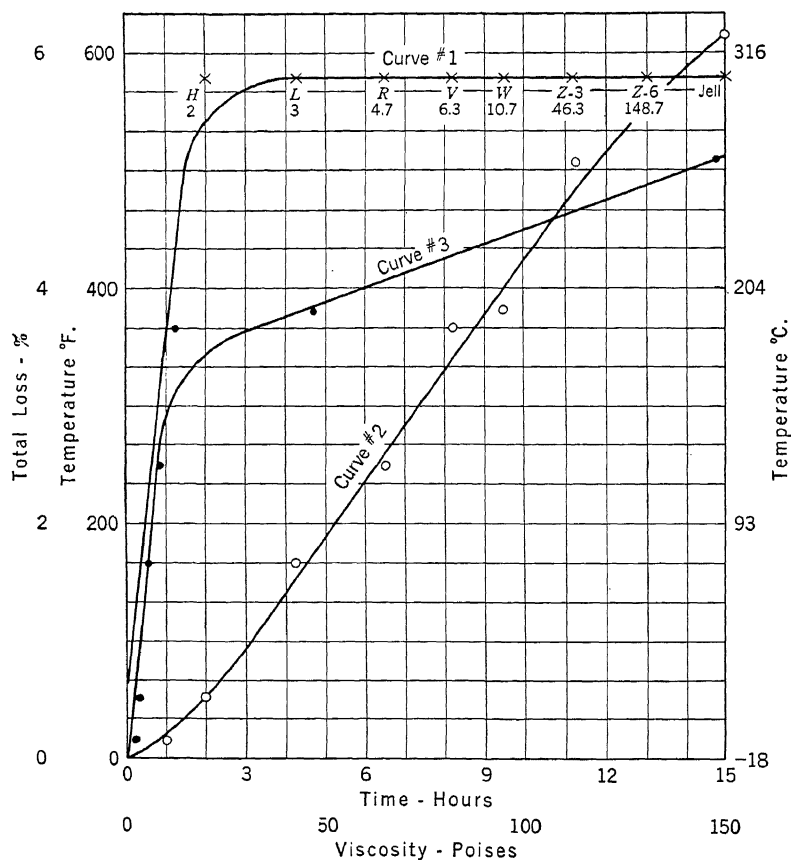


FIG. 17. Percentage of Loss during Heat Bodying of Alkali-Refined Linseed Oil.

Curve 1—Shows the relationship of the rate of rise of temperature and top processing temperature versus time of cooking. On this curve is indicated the viscosity developed by the linseed oil as the processing time increases; the viscosities are given both in the Gardner-Holdt Scale and in poises. The poises are given in approximate values.

Curve 2—Indicates the total loss of linseed oil in per cent versus processing time.

Curve 3.—Indicates the total loss in per cent versus the approximate viscosity.

driven off during the heating up period, and the later fuming is caused by distillation of thermal decomposition products formed during the bodying period.

The above figures show that an average 5 to 10 per cent loss per batch represents a substantial economic loss of valuable raw materials. So far there is no satisfactory fume recovery process available, but the prospect of converting net material loss plus disposal expense into possible profit is attractive enough to spend some time and money on fume recovery research.

The present methods of fume disposal may be roughly divided into two groups: complete destruction by combustion and separation by liquid treatments.

Disposal of fumes by combustion requires a minimum of equipment, assures complete fume elimination from atmosphere, and in correctly designed incinerating furnaces the process consumes very little fuel. However, incineration of hot combustible vapors, though very simple, calls for special design features to safeguard against flame propagation in the opposite direction of the flow of vapors between kettle and incinerating furnace. Mixture of a combustible gas or vapor is inflammable only under certain conditions of concentration and may be rendered more or less inflammable or even non-inflammable, depending on the combustible vapor-air ratio.

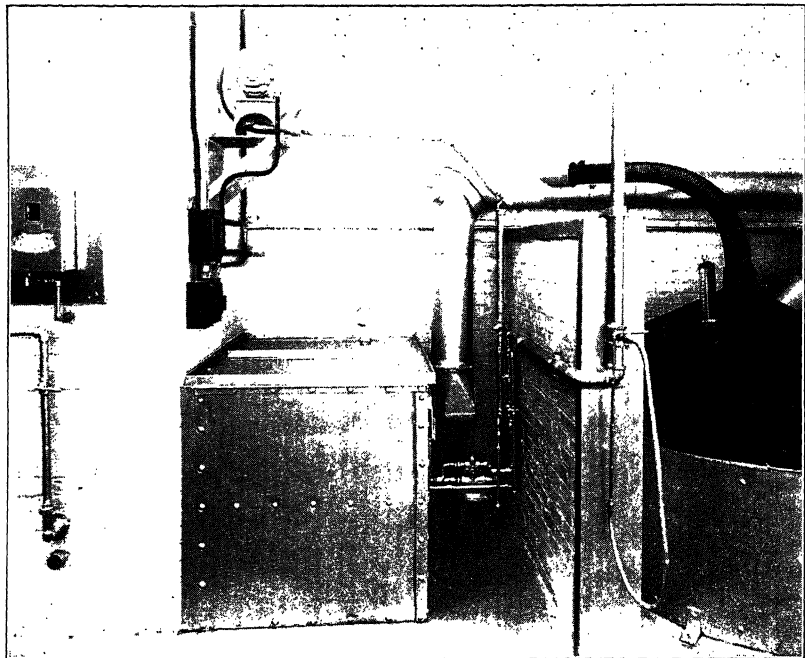
When the combustible particles are so widely separated that those set on fire by the igniting medium will not set fire to those that are nearest, the mixture is called too "lean" for combustion and will not burn. When the combustible particles are so close together that they exclude the oxygen necessary for combustion, the mixture is called too "rich" and it will not burn. The concentration or percentage by volume between the leanest and richest mixture that will burn is called the "explosive range." Between the minimum and maximum limits of the explosive range are found various phases of slow and rapid combustion.

This range of inflammability between the limit mixtures is different for each combustible substance and in many cases only a few per cent apart. To illustrate this narrow range of inflammability we need only to think of automobile carburetor adjustment, where slight change in gasoline vapor-air ratio gives power or failure.

As shown by work of Eberly and Mattiello, incineration of oil and varnish fumes deals with an inflammable fume-air mixture of variable concentration. At the start of the fume-producing period evolution of fumes increases at an advancing rate to some maximum point and



slows down near completion of the process. Obviously the safest way of burning fumes of such variable concentration is to introduce sufficient air directly at the point of origin, i.e., at kettle outlet, and so maintain the fume-air ratio below its lower explosive limit, through the entire cooking period. Such dilute mixture may be safely con-



*Courtesy of Kiente and Co.*

FIG. 18. Paint and Varnish Fume Incinerator, Gas-Fired. Built by Morse Boulger Destructor Company.

veyed to the incinerating furnace and simply consumed by additional fuel.

Incinerating furnaces can be designed to suit any varnish plant capacity and are generally rated in pounds of fumes per hour. The selection of suitable furnace capacity depends largely on production schedules. In a small plant where one varnish maker takes care of three to four 100-gallon kettles, starting each batch say one-half hour to one hour apart, a single incinerator capable of consuming 60 to 80 pounds of fumes per hour is large enough. For approximate estimate, each 100 gallons of varnish batch or 250-gallon oil batch requires about 15 pounds of fume incinerator capacity. In some plants where

production per fire varies from day to day it may be advantageous to install small individual incinerators; this is a question of balancing fuel cost against investment cost. A correctly designed incinerator, constructed of light-weight insulating refractories, should consume not more than 500,000 Btu of gaseous fuel or 800,000 Btu of liquid fuel per each 15 pounds of fumes per hour. The indicated difference in fuel consumption between gaseous and liquid fuels is not due to any difference in combustion efficiencies, but is simply due to larger combustion space required by liquid fuels. Consequently larger furnace volume has to be maintained at incinerating temperatures.

The question of proper furnace temperature required for complete fume incineration is largely a matter of opinion. Some incinerator builders insist on high temperatures ranging around 2000° F.; others maintain that a lower range, around 1400° F., is sufficient.

A recently completed investigation by the author based on experimental data covering a large variety of individual fumes showed that the majority of fumes and obnoxious vapors can be completely deodorized and decomposed in the presence of air when raised to temperatures ranging from 750 to 1200° F. Oil and varnish fumes were found to be completely oxidized when introduced as a 1 per cent fume-air mixture entering the combustion zone of a gas-fired incinerator at 180° F. inlet temperature and leaving the furnace at 1120° F. Although this temperature range, when compared with existing fume incinerator practice, may seem unusually low, it agrees well with published data on ignition temperatures.

## Conclusion

It may be truly said that the paint industry grew up to its present state of perfection by hard work. Manual labor and careful watching were chiefly responsible for early advances in the heat processing of vehicles when wood, coal, coke fires, and hand-stirred portable kettles represented the customary cooking room equipment. The products were considered of first-class quality, and indeed were so accepted as long as there were no adequate scientific means to show otherwise.

The perfection of new test methods and of delicate test instruments, plus simultaneous development of synthetic materials, led to the demand for more accurate cooking processes. We now speak of two, three, or more molecule polymerization products in definite percentages per given batch of bodied oil and insist that these percentages be duplicated with heretofore unknown exactness.

Today, manufacturers of cooking room equipment are asked to guarantee heating performance under most critical temperature-time cycle conditions and are fully prepared to meet these demands. Portable kettles, heated by hand-charged solid fuels, are hardly adequate to produce high-quality synthetics and carefully prescribed viscosities of bodied oils. The present-day trend is toward large-capacity well-insulated stationary kettles equipped for mechanical agitation and heated by a modern temperature-controlled heat source.

There is no universal answer to the often-discussed question of which heat source is preferable to others. We generally get what we pay for; the more refined is the heat source, the greater is its value and the better is its performance. To summarize the so-called advantages and disadvantages of each would be repetition of so many sales arguments. The logical way to proceed is to draw up performance specifications for each heating operation and submit those to heating equipment specialists for recommendations. The final decision of a suitable heat source should be primarily based on performance characteristics, ease of control, and overall operating cost per unit weight of product. The often stressed unit Btu cost of fuel or energy is misleading, and of no value as it alone represents only a portion of the total heating costs.

Just what the future developments in heat processing will be is anybody's guess. One outstanding trend in most industries is to continuous line productions methods, which invariably give greater hourly output, lower labor costs, and products of uniform quality.

There are several possibilities that suggest continuous \* production for heat processing of liquids: continuous straight oil film heating in atmosphere of inert gases for bodied oils; continuous varnish production by film heating of colloidal suspensions of gums and other solids in oils; thermal treatments of oil films by heat rays of suitable wavelength.

In addition to economic advantages, the continuous heat processing of liquids in thin layers would be under exact control of temperature-time gradient, and may produce materials of radically different physical characteristics. Whether such methods and the resulting material would be to advantage over present batch-treating systems can be determined only by intensive research.

\* *Editor's note:* See "Polymerization Methods of Drying Oils," Chapter 2, for already existing methods of continuous heat process for bodying tung oil.

## CHAPTER 8

### VARNISHES

FREDERICK M. DAMITZ, JOHN A. MURPHY, and JOSEPH J. MATTIELLO

#### HISTORY

The Oxford English dictionary (1916) states that the origin of the word varnish is unknown. The legend put forth by a great many authors is fitting and proper for such an interesting and important industry. In ancient Egyptian history we are told of a woman named Berenice, whose grandfather was a half brother of Alexander the Great and whose descendant was Cleopatra. Berenice had extraordinary golden hair. During one of the conquests she said that if the king did not return safely, she would cut off her golden locks. She kept her promise and, as the myth goes, the locks were carried by the comet to the sky and formed the Milky Way. Later, after one of the Egyptian conquests of foreign land, the warriors brought back amber, which, because it resembled the beautiful golden hair of Berenice, was called *berenice*. The logical sequence in name is supposed to have been: *berenice*, *verenice*, *vernix*, and *varnish* (Mediaeval Latin). *Berenice* or *verenice* is given as the common name for amber in the Middle Ages. After the sixteenth century the name *vernix* ceased to be applied exclusively to the dry resin, but was used to denote the fluid compound of amber and oil or resin and oil. Today the general term "varnishes" applies to compositions of resins, oils, driers, and thinners, or resin and thinners. For more historical data, see the historical chapter at the beginning of Volume I.

#### SCOPE

Varnish films tend to preserve and beautify the surface to which they are applied. In many cases, the varnish film improves the usefulness of the material on which it is applied, i.e., coating fabrics for insulation, for making rain coats, umbrellas, etc.

Varnish making is a skilled art which, for many years, has had a place as one of the necessary and outstanding industries in the United

States and in Europe. Recent years have seen this industry grow by leaps and bounds because of the development of so many new raw materials which are adapted to varnish making. These new raw materials possess properties that have permitted the use of the finished varnish product in fields previously untouched by the varnish industry.

Extensive research work in the science of resin manufacture and of varnish manufacture itself has gradually thrown more light on the reactions involved in processing varnishes. This gives to the skilled varnish formulator additional data from which he can visualize his work and use his skill to advantage. Varnishes have been used in the past mainly for decorative and protective purposes and, in some instances, for chemical resistance, electrical insulation, and utility purposes. Today, they have these same uses. With modern scientific research, the use of new type varnishes has spread to practically every field of endeavor. In every-day life, no matter how small or large the enterprise, evidences of the uses of varnishes or coatings are quite apparent. The terms coatings and varnishes are used interchangeably in this chapter.

### DEFINITIONS

The definition of a varnish, as given by one of the technical societies, is: "A liquid coating material containing no pigment which flows out to a smooth coat when applied and dries to a smooth, glossy, relatively hard, permanent solid when exposed in a thin film to air."

There can be no doubt that varnishes are a heterogeneous system, consisting of resin and thinners, or resins, oils, thinners, and driers. Some schools consider varnish a solution; others classify it as a colloid.

In a physical sense varnishes are fluids that can be spread readily to thin smooth films which dry to hard, continuous, permanent, solid coatings when exposed to air or heat. The first step in the drying of varnish films is the evaporation of the volatile portion, which leaves the non-volatile material to dry by oxidation, and/or a combination of polymerization and condensation. Some varnishes dry only by evaporation, for example, cold-cut resin varnishes, shellac, and chlorinated rubber types.

### CLASSIFICATION

According to their constituents, varnishes may be divided into two types:

- A. Oleoresinous varnishes
  - (1) Oil plus
    - (a) Natural resins
    - (b) Synthetic resins
  - (2) Oil
  - (3) Oil-modified
    - (a) Glycerol phthalate
    - (b) Chlorinated rubber
- B. Spirit varnishes
  - (1) Solvent plus
    - (a) Natural resins
    - (b) Synthetic resins

Group *A* dries by oxidation, or oxidation and condensation, or by oxidation, condensation, and polymerization. Group *B* dries either solely by evaporation or by evaporation and some polymerization.

### OLEORESINOUS VARNISHES

#### General Composition

The four main constituents (raw materials) of the oleoresinous varnishes are:

- (1) *a.* Drying and semi-drying vegetable oils.
  - b.* Drying and semi-drying fish oils.
  - c.* Oils chemically converted from non-drying to drying type.
- (2) Resins.
- (3) Driers.
- (4) Thinners (or solvents).

These are illustrated diagrammatically in Table I.

#### Function of Each Constituent

The *resins* impart hardness, toughness, ductility, adhesion, waterproofness, and gloss. Hard resins accelerate drying.

The *oils* impart flexibility, toughness, adhesion, durability, and relative waterproofness.

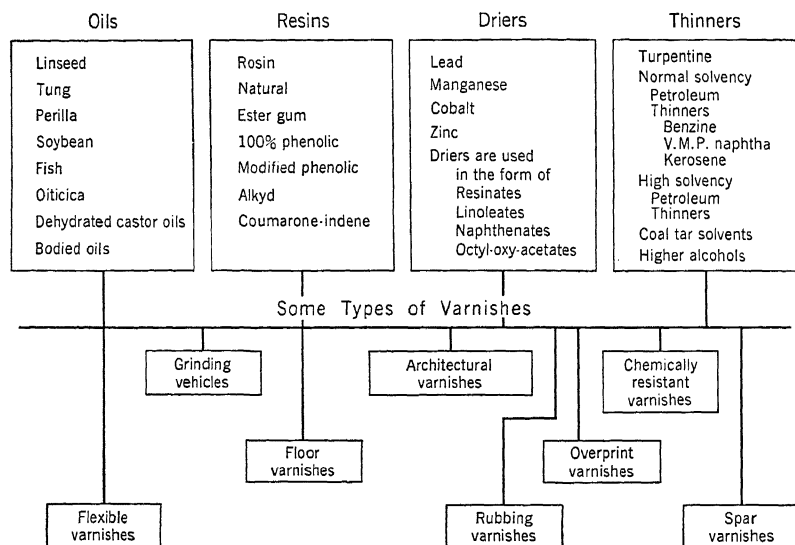
The *driers* have, as their main function, the acceleration of the drying time. For example:

Linseed oil requires approximately five days to air dry by itself when flowed out to a thin film, but, with the proper combination

and amount of drier, it will dry within as brief a time as three to five hours.

The primary function of *thinners* is to reduce viscosity or increase fluidity so as to permit easy application of the varnish coating. Slow-evaporating solvents also have the effect of increasing hardening of a film. When resins and oils are processed together (cooked), a very viscous substance is obtained which is difficult to spread into a thin film. In reducing the viscosity, the thinners or mixture of thinners used must satisfactorily dissolve or disperse all the solid ingredients of the varnish. This is true in general for all vehicles.

Table I  
Composition of Oleoresinous Varnishes



### Characteristics of Oleoresinous Varnishes

In designing a varnish, it is absolutely necessary to know the performance expected. For example:

1. *Floor varnish*—must dry overnight to a tough, hard film of good gloss; must have good water and alkali resistance and good resistance to scuffing.

2. *Spar varnish*—should dry to a hard, glossy film which must stand the atmospheric conditions prevailing—salt air, actinic rays of the sun, moderate chemical resistance, etc.

3. *Chemically resistant varnishes*—must be designed to withstand acids, alkali, and other chemicals with which they may come in contact.

4. Many other examples, each to meet some special requirements.

### Varnish "Oil Length"

A varnish may be composed of one of each of the components enumerated; however, most varnishes are composed of several resins, oils, driers, and thinners.

Varnishes are known as of short, medium,  
or long "oil length."

The oil length is defined as the number of gallons of oil used per 100 pounds of resin. Varnishes of short oil length will dry faster and will be more brittle usually than varnishes of long oil lengths.

Table II illustrates a 45-gallon varnish, spar varnish type, and an 18-gallon varnish, floor varnish type.

TABLE II

#### *45-Gallon Varnish (Spar Varnish Type)*

Basis: 100 lb. resin	} Varies from 45 to 60%
45 gal. oil	
$x$ gal. or lb. drier	non-volatile
$y$ gals. thinner	} Varies from 55 to 40%
	volatile

#### *18-Gallon Varnish (Floor Varnish Type)*

Basis: 100 lb. resin	} Varies from 45 to 50%
18 gal. oil	
$x'$ gal. or lb. drier	non-volatile
$y'$ gal. thinner	} Varies from 55 to 50%
	volatile

### General Manufacturing of Oleoresinous Varnishes

Natural hard resins such as kauri and congo are insoluble in linseed oil, tung oil, and other drying oils. It is necessary to heat the resin (this is discussed in greater detail later in this chapter) to a temperature above the softening point, whereupon decomposition and depolymerization take place. This causes a loss in weight from 15 to 30 per cent, depending upon the hardness of the natural resin. The resulting fused resin is soluble or reacts readily with linseed oil and other drying oils under the influence of heat. The oils are added in either the raw or bodied state. With many of the synthetic resins, the oils and resins



are added together to the kettle. The resin and oil combination is heated until a homogeneous mass is obtained.

In many cases, a small amount of either raw or bodied oil is added as a chill-back, to cool the hot mass of resin and oil quickly. Now the batch of varnish is ready for thinning, and, while thinning, driers are added. The varnish is next clarified by filtering or centrifuging, stored, and, whenever necessary, aged.

### Testing

Varnishes are usually examined by the manufacturer for appearance (clarity), color, viscosity, specific gravity, drying time, etc. With some varnishes, it is necessary to check their water, alkali, and acid resistance. Rubbing varnishes should be checked for rubbing and polishing; and insulating varnishes, for electrical insulating properties. Some varnishes may have to be resistant to specific reagents.

### Application

Varnishes are applied either by brushing (mainly for painting homes and buildings) or by spraying or dipping (mainly for commercial uses).

### Uses

Varnishes are used on surfaces either for interior or exterior exposure and on many hundreds of industrial articles.

### Oils and Their Classification

The first recorded use of vegetable oils in varnishes, comparable to our present method of varnish formulation, is credited to Jacobus Tholeto in 1440. In this section we do not describe at any great length the source, refining methods, or the chemistry of the drying oils. For such information, see Chapters 1 to 6, inclusive, in Volume I.

The oils are classified into two main divisions, the drying and the semi-drying oils. In the first group are included some vegetable, some fish, chemically converted, and synthetic oils. In the second group there are some vegetable and some fish oils.

**Drying Oils.** Linseed oil is used in varnish making in larger quantities than all the other oils combined. Raw linseed oil, as pressed from the flax seeds, contains a very small quantity of intimately incorporated mucilaginous albuminate commonly called a "break." This break must be removed from the raw oil because, if the oil is used as a grinding oil, it will darken the light pigments; or, if the oil

is used as a varnish oil, the break coagulates and chars, darkening the color of the varnish.

We now have on the market, for use in varnish making, various semi-refined and refined raw linseed oils, known generally as improved raw, non-break, alkali-refined, acid-refined, and varnish oil. In addition to these, there are other specially prepared raw oils, known as boiled and oxidized (blown) oils.

*Improved raw linseed oil* does not "break" at any temperature, and has an acid number of 4 to 6. It is used in the production of driers and many finishing and grinding varnishes where economic consideration is more important than the color of the vehicle. This oil may also be used as a grinding oil.

*Non-break linseed oil* is the same type as the improved raw; it does not break and has a relatively lower acid number of 2 to 4. It can be used for making the same variety of varnishes as the improved raw, but where low acid number is more desirable.

*Alkali refined linseed oil* is practically neutral (acid value less than 0.5) and is a very important oil. It is used quite extensively in the varnish industry for making of pale varnishes and pale vehicles for white and lighter-colored paints and enamels.

*Varnish linseed oil* is an alkali refined linseed oil with an acid number of 2 to 3. It has good bleaching properties and is recommended for general use in varnishes.

*Acid-refined linseed oil* is used mainly as a grinding liquid for basic carbonate white lead. It is also used to some extent in varnishes.

*Oxidized linseed oil* (also known as *aged oil*) is a regular or amber-colored oil, from which the break has been removed by passing air throughout the oil and by heating it at low temperature for a relatively long time. This is a rapid-bodilying oil which is used in varnishes where color is of no consequence.

*Boiled oil* was first made by heating raw linseed oil to which litharge had been added to a temperature of 525–550° F. This oil is generally known as crude boiled oil. It is considerably improved in drying property but is dark in color and muddy, owing to the suspended lead salts. Later, oxides of lead and manganese were added to the oils. These metallic oxides are at present displaced by soluble driers, such as resinates, linoleates, and naphthenates. Modern practice is to heat an alkali refined linseed oil to a temperature of 550° F., shut off the heat, and add the soluble driers as the oil is cooking. The driers are thoroughly dissolved or dispersed in the oil. The resulting product is a very pale oil, and this is the boiled oil of modern :

*Perilla oil* is, chemically, closely similar to linseed oil. In the raw state it has a tendency to crawl, but this is eliminated by heat bodying. This oil can be refined and used similarly to linseed oil. It is, however, faster-drying and bodies or increases in viscosity under heat more quickly than linseed oil.

*Tung or China wood oil*, next to linseed oil, is used in varnish making in larger proportion than all the other drying oils. This picture is changing, however, and other oils are coming into extensive use. It is quicker-drying and faster-bodying than either perilla or linseed, and it has decidedly better water resistance. Until the advent of phenolic synthetic resin, the first improved spar varnishes were made of tung oil and ester gum. Tung oil has been used extensively in the quicker-drying so-called four-hour varnishes.

*Oiticica oil* resembles tung oil in many of its physical and chemical properties. Oiticica oil dries more rapidly than linseed and perilla, but more slowly than tung oil. Its bodying rate or increase of viscosity under the influence of heat is also faster than linseed and perilla oil. Oiticica oil, at processing temperature, bodies faster than tung oil up to the point near gelation, then tung oil bodies considerably faster. In many varnish formulations, oiticica is replacing a portion of the tung oil. With some phenolic resins, oiticica oil varnishes can be made which have satisfactory outdoor durability.

*Fish oils* used as drying oils in the coating industry are obtained from the menhaden, sardine, and pilchard. The crude oil is refined by the removal of the highly saturated fatty acids, usually by refrigeration.

*Dehydrated castor oil* is a good partial substitute for tung oil, and its general use is increasing. It appears to have a promising future and should be studied for its own value. It is presented in greater detail in Chapter 4, Volume I.

**Semi-Drying Oils.** *Soybean oil* is a semi-drying oil used in admixtures with linseed, tung, perilla, oiticica, and dehydrated castor oil in varnishes. It is quite likely that further research in the use of this oil will increase its consumption in the paint industry. In Chapter 6B those resins which are specially reactive with these oils are discussed.

*Hempseed, sunflower, and safflower oils* are used in varnishes only to a limited extent in admixtures with other oils.

**Bodied Oils.** The raw or refined and bodied drying and semi-drying oils are used in oleoresinous varnishes. Generally speaking, bodied drying oil films dry more quickly, are tougher, and have better water, alkali, and chemical resistance than raw oil films. They are used in

varnishes in an effort to reduce the bodying or cooking time, and to impart the inherent qualities of bodied oils. The semi-drying bodied oils are also improved in these properties over the raw oils. Owing to slower drying of these oils, they retain their apparent elasticity for longer periods than the drying oils. See Chapter 4.

**Resins.** Resins play a very important part as constituents of varnishes. Resin may be defined as a semi-solid or solid, complex, amorphous mixture of organic compounds with no definite melting point.

Resins are divided into two main groups—natural and synthetic—which may be further classified into a great many groupings as to composition, reactivity, function, etc. The natural resins are discussed in detail in the chapter on natural resins; the synthetic resins, such as alkyd and phenolic, are discussed according to their composition in separate chapters. All these chapters are in Volume I.

**Natural Resins.** Such natural resins as dammar, kauri, copal, congo, east india, and amber were the first important varnish resins to be used in the varnish industry. These resins are discussed in detail in Chapter 8, Volume I.

**Ester Gum.** The first synthetic resin of practical importance was ester gum, which came to prominence about 1900. Ester gum ranges from a soft plastic material to resins of high melting point with acid numbers of 8 to 16. These resins still enjoy an important place in the paint, varnish, lacquer, and ink industry. See also Chapter 10, Volume I.

**Phenolic Resins.** After the ester gum resins came the modified phenolic resins. With these, a considerable advance was made in producing varnishes, improved in outside durability, toughness, gloss retention, etc. These resins were introduced in Europe around 1916, and in the United States about 1922. They are made by modifying the phenol and formaldehyde condensation product during the processing with rosin, rosin esters, or natural resins to produce resins which are soluble in vegetable oils. The modified phenolic resins combined with tung oil formed the basis of the first modern four-hour coatings.

Next appeared the concentrated 100 per cent oil-soluble phenolic resins which found their place in the varnish industry about 1928–1929. These groups of resins have been expanded so greatly that they have been given the name “tar acid resins.” The phenolic resins may be divided into three general classes:

Modified phenols—Phenol-formaldehyde condensation products rendered oil-soluble by chemical combination or physical dispersion in other materials such as rosin and copal.

Unmodified or 100 per cent phenols—Condensation products made from tar acids other than simple phenol, which are themselves soluble in drying oils and thinners.

Substituted phenols—Products from the condensation of the substituted phenols and formaldehyde.

See Chapter 12, Volume I.

**Coumarone—Indene Resins.** They were introduced in the United States between 1915 and 1920; about the same time the modified phenolics were being introduced in Europe. These resins vary in types as to melting point and color; they are neutral, non-oxidizing, and unsaponifiable. To varnishes, they impart inertness, adhesion, and good electrical properties. These resins are discussed in detail in Chapter 14, Volume I.

**The Alkyd Resins.** Oil- and resin-modified alkyd resins became of commercial importance to the varnish industry in 1928 or 1929. This group of resins are condensation products synthesized by reacting polyhydric alcohols such as glycerol and the glycols with dibasic organic acids such as phthalic, maleic, succinic, sebacic, and carbic. These condensation products are almost always modified to give the properties desired. The modifying agent may be drying, semi-drying, or non-drying oil, the fatty acid of an oil, a natural resin such as rosin, a synthetic resin of the phenol-formaldehyde group, urea-formaldehyde resins, or other substances. Alkyd resins are discussed in greater detail in Chapter 13, Volume I.

**Urea-Formaldehyde Resins.** The successful use of urea resins (see Chapter 15, Volume I) in the paint and varnish industry is only recent. These resins are generally marketed as water-white viscous solutions in a mixture of organic solvents (mixture of butyl alcohol and xylol). They are used mainly in baking finishes. They can only rarely be used alone because the cured resin is hard, brittle, and lacks adhesion. When combined with drying or non-drying alkyds, they produce coatings which when baked are marproof, resistant to alcohol, grease, oil, fruit acids, etc. Because of their colorless properties, beautiful pastel colors can be obtained which are not discolored on aging, making these combinations suitable for metal finishes on toys, refrigerators, can coatings, stove parts, bathroom and hospital appliances, bicycles, motors, machine parts, etc. These coatings render textiles crease-, grease-, and water-resistant; and they render paper water- and oilproof. They are also used in drinking cups, food containers, packaging papers, etc., because of the low permeability with

highly penetrating oils, and tasteless, odorless, and non-toxic properties.

**Vinyl Resins.** Polymerized vinyl acetate, the first prominent vinyl resin of industrial importance, appeared about 1912. Films of polyvinyl acetate do not discolor by exposure, and after irradiation they become opaque to ultraviolet light. They are hard and tough and can be used in heat-sealing coatings. Aldehyde-treated polyvinyl acetate resins have come into the industry lately, and have been made into spirit type varnishes, lacquers, and enamels that will stand exposure to weather. The higher aldehyde-treated polyvinyl acetates produce baking varnishes of exceptional qualities.

The copolymers of vinyl acetate and vinyl chloride have found extensive use as lithographic varnishes and enamels and coatings for all types of bases, such as cloth, silk, and paper. The polyvinyl chloride has been used as a rubber substitute in many industries, being applied mostly in solution form. The polyvinyl chloroacetate resins have been used chiefly in Europe as surface coatings, whereas the polyvinyl chlorides have been used to a greater extent in the United States. See also Chapter 17, Volume I.

**Rubber Condensation Derivatives and Chlorinated Rubber Resins.** These types of rubber resins have been offered to the varnish industry. The former type was marketed commercially around 1932, the latter was used in Europe for a good many years prior to its adoption in the United States in 1934.

The rubber condensation derivative resins (see Chapter 18A, Volume I) are, as a whole, true thermoplastic resins, resistant to most acids, all alkalies, and solvents of the ketone type, and soluble in gasoline and benzene. They are exceptionally resistant to moisture, alkali, and possess good electrical properties. They are tasteless and odorless. Some forms of these resins can be molded direct; other forms can be used as varnish resins. They may be cold-cut and plasticized to form solvent type varnishes or may be added to oil varnishes by cold blending. These resins may be cooked directly with oils, and they may be blended with wax and plasticizers to form hot melt solutions.

**Chlorinated Rubber** (see Chapter 18B, Volume I). This is supplied in several viscosities, ranging from 5 to 2,000 centipoises; it is stable under normal conditions, light-fast, clear, odorless, tasteless, non-toxic, non-inflammable. It is soluble in aromatic and chlorinated hydrocarbons, hydrogenated petroleum, esters, and most ketones. It is compatible with many of the lacquer plasticizers and with vegetable

oils. The chlorinated rubbers can be used as solvent varnishes reinforced with other resins and plasticizers. They can be blended with oil varnishes and with drying oils. They impart to varnishes inertness, alkali resistance, and resistance to moisture penetration.

**Acrylic Resins.** These are of the newer types offered to the paint and varnish industry (see Chapter 19, Volume I). In the last ten to fifteen years, a suitable commercial method has been developed for the production of these resins. They were introduced into the coating industry about 1935. These resins range from soft, sticky, semi-liquids to hard, tough, thermoplastic solids. They are colorless, transparent, stable under exposure to heat, light, and oxidizing agents, and thermoplastic. Solutions of these resins in toluol and similar solvents make them applicable as undercoats in difficult adhesion jobs and in textile and paper coatings.

**Polystyrene Resins.** They are thermoplastic products discovered about 100 years ago and are the oldest synthetic resins known. Their practical application has been delayed because of cost and difficulties in manufacture. Polystyrene resins were prepared in Europe and imported here in small quantities as early as 1933. These resins were extremely high in price and therefore could not be used by the trade in general. Production of these resins in the United States was started early in 1937, and their price was abnormally high. Later in 1937 and in 1938 greater activity in the production of these resins became apparent, and numerous polymers of many different molecular weights were offered to the consuming public at prices which were within reach of the specialty manufacturer. Polystyrene resins are clear, colorless, odorless, thermoplastic, moisture-resistant, inert, and possess exceptional electrical properties. The newer polymers offer resins that can be utilized in the coating industry to great advantage. The most recent development in the *styrol resins* is the oil-soluble type which can be kettled in the varnish oil. The alkaliproofness and color should prove of some real advantage.

**Other Resins.** Finding their way into the varnish industry are:

1. *Petropol resins (Petropols)\** are petroleum resins obtained in the higher temperature vapor phase cracking operation. They are discussed in detail in Chapter 20, Volume I.

2. *Chlorinated diphenyl* resins are made by chlorinating diphenyls (see Chapter 20, Volume I). They were prepared commercially about 1928. They range from water-white mobile liquids to pale yel-

\* Trade name.

low transparent solids. They are non-drying, non-polymerizing, non-oxidizing, fire-retardant, alkali- and water-resistant. They combine with vegetable oils, possess good electrical properties, and are used in wire insulation as saturants in asbestos cables and as fire retardants and plasticizers in fireproof nitrocellulose lacquers.

3. *Furfural resins* are phenyl aldehydes. They are dark in color. Their principal uses have been in molded articles, where they have great dimensional accuracy, and in a few specialties in the varnish industry.

4. *Aryl sulfonamide-formaldehyde resins* are condensation products of aryl sulfonamide and formaldehyde or other aldehydes, which are discussed in Chapter 21, Volume I. They are colorless resins which are used chiefly in the lacquer industry.

5. *Hydrogenated rosin* and rosin esters are finding their way into the varnish industry. They possess unique compatibility properties and are worthy of investigation.

6. *Monocyclic ketone* condensation products have been known for a long time, but patents for the production of these resins did not appear in the United States until 1920. The resins, as a rule, are neutral, unsaponifiable, light-fast, and soluble in most organic solvents and in drying oils. They are compatible with nitrocellulose. When cooked with oils, slight decomposition takes place. Their hardness is limited, but their weather resistance is unusually good, even in short oil varnishes and enamels. They do not decrease the brushability of enamels.

7. *Polymethylene polysulfide* reaction products have been used extensively in the rubber industry. They are insoluble in paraffin hydrocarbons and vegetable oils. They are affected only slightly by coal tar and most lacquer solvents. Because of these properties, they are used in solvent type varnishes and paints where chemical resistance is desired.

8. *Cashew resins* prepared by the action of aldehydes on cashew shell liquid alone or on fractions of cashew shell liquid. (See Chapter 2, Volume I.)

9. *Synthetic resins from melamine* are thermosetting and possess the properties of urea resins, such as hardness, gloss, mar resistance, and color permanence. They differ from urea in that the whites and pastel shades can be baked to a hard film at higher temperatures than similar urea enamels without discoloration or loss of luster. They may also be cured as low as 180 to 220° F. (82.2–104.4° C.) with speed and film qualities of previous urea combinations baked at 275 to 325° F. (135–162.8° C.). These resins produce enamels of out-



standing resistance to water, alkali solvents, and greases in comparison to other non-yellowing finishes, especially of the thermosetting type.

10. Terpene resins are finding many uses in varnishes. These are discussed in pages 567-569, Vol. I.

### Driers

It has already been mentioned that the main function of driers is to accelerate the drying or hardening of a film.

**Types of Driers.** The most effective driers are compounds of cobalt, manganese, and lead. In the past, red lead, litharge, burnt umber, cobalt acetate, and manganese hydrate have been added to varnishes during the early stages of processing. Today they are used in form of resinates, linoleates, naphthenates and octyl oxyacetates, mainly in the liquid state, and are added to varnishes during the thinning stage. Driers are discussed in greater detail in Chapter 22, Volume I. Additional information is given in Chapter 27, Volume II.

**Strength of Driers.** Cobalt, the strongest of the three, is a "surface" drier; manganese, next strongest, is also a surface drier; and lead, the least strong, is a "through" drier. In the formulation of paint, varnish, or other surface coatings, great care must be exercised in the choice and amount of drier to be used.

**Lead Drier.** This, the most widely used of the driers, is employed invariably in combination with small amounts of cobalt or manganese, or small amounts of both.

Lead drier produces films intermediate in hardness between cobalt and manganese.

**Manganese Drier.** This drier is used alone or in combination with lead and cobalt. In those varnishes used for making white enamels, it has a tendency to impart a pink coloration, even when used in very small amounts—just sufficient for drying. Of the three driers, it produces the hardest film.

**Cobalt Drier.** This drier is used to a great extent in varnishes, and particularly in those varnishes which are used for the making of white enamels, since it does not relatively discolor these products. Excess amounts of cobalt will cause discoloration. It is very often employed alone, and sometimes in combination with lead, or manganese, or combinations of both of these.

Cobalt drier gives rise to skinning trouble, owing to its fast surface-drying action. This difficulty is used to advantage in wrinkle and crystal finishes.

Its drying is similar to that of manganese, but provides a more elastic film.

*Note.* There is an optimum amount of drier which should be added to varnishes or other vehicles, above which the driers not only become ineffective but actually retard drying. Too much drier causes the loss of gloss in enamels and a lessening of the durability.

Driers are added to oils or vehicles on the basis of the percentage of the metal to the amount of the oil employed in the vehicle. The general amounts of these driers have been given as:

Cobalt metal .....	0.02%
Manganese metal .....	0.05%
Lead metal .....	0.50%

Some representative figures for the amounts of cobalt and lead to be used in varnishes employed for making white paints are:

	1	2	3
Cobalt metal .....	0.025%	0.015%	0.005%
Lead metal .....	None	0.20%	0.25%

A drier composed of the three metals for general use in varnishes for colored enamels:

Cobalt metal .....	0.01%
Manganese metal .....	0.03%
Lead metal .....	0.20%

Besides these three metals, iron and zinc are next in importance as driers. They and other metals are discussed in detail in Chapter 22, Volume I.

### Thinners—Solvents

A thinner is generally thought of as a paint and varnish ingredient whose function is only to decrease the viscosity, thus increasing the fluidity of a paint or varnish so that it can be spread more easily. This is, of course, one of the primary functions of a solvent, but only one of them as viewed by the varnish technician. Solvents must be chosen with great care, especially when formulating varnishes for specific projects which have to meet rigid specifications.

A definition generally accepted, covering a given group of solvents, is: A volatile or thinner solvent may be defined as an organic liquid which can be distilled without decomposition, evaporates completely at ordinary temperature, and has excellent solvent power for oils,

resins, and other vehicles employed in the varnish industry. This is a good definition for a volatile solvent and covers probably 90 to 95 per cent of the solvents used. For modern paints and varnishes, however, we have to consider not only the volatile solvents but also the partially volatile and non-volatile solvents which play an important part in the baking of varnishes and enamels.

The modern formulator must design his paint, varnish, and enamel products so they may be spread into thin films by brushing, dipping, spraying, roller coating, or knife coating on many different surfaces or bases—wood, metal, laminated Bakelite, cardboard, paper, silk, rayon, etc.—and so they may be dried to a solid film at ordinary atmosphere (so-called air-dried), at definite humidity and temperature, or by baking at various temperatures for definite periods of time. Because of the many types of modern baking equipment employed by the large user of paint, enamel, and varnish products, the solvents used are not limited to those which were normally considered to be volatile at room temperature. The scope of solvents has broadened to include the high-boiling solvents, the partially volatile solvents, the non-volatile solvents (a type of plasticizer, extender, or stabilizer), and the hot solvents (a group of solvents which swell typical resins to such an extent that they are a gel at room temperature, but become fluid at elevated temperatures and are used as a coating medium at specified temperatures).

Here are given a number of factors, or properties, which a solvent should possess in addition to that of reducing viscosity of a paint product to usable consistency:

1. It should completely disperse all the constituents of a vehicle to insure compatibility necessary in obtaining a homogeneous film.
2. It should be non-hygroscopic.
3. It should have a controlled evaporation rate.
4. If it is partially non-volatile, it should have a definite non-volatile content.
5. In most cases, it should produce a low viscosity with high film-forming (non-volatile) solid content.
6. It should be stable and not have a *continued action* on the constituents.
7. It should stand considerable dilution (as in the case of extenders in cotton solutions and the addition of cheaper diluents in short-oil synthetics).

8. It should have good solvent power in the higher ends to produce compatibility in the final laying of the film.

9. It should have a minimum amount of solvent retention.

10. It should have a uniform rate of evaporation under the coating conditions so as to allow the film to heal during and after evaporation.

These foregoing properties are seldom found in one solvent, but are obtained generally by two or more solvents. Because of this fact, the use of solvent combinations in the specialty coating field has passed the rule-of-thumb stage and is becoming a science.

Some forty years ago, turpentine was the only thinner of importance in the paint industry. In the course of years, others came into prominence, the petroleum hydrocarbons of normal and high solvency type, coal tar solvents, hydrogenated solvents, esters, ketones, ethers, chlorinated solvents, alcohols, alcohol ethers, and others.

**Turpentine.** Being the first thinner to be used in the paint and varnish industry, turpentine has always been associated with paints because of its odor. Turpentine has higher solvency than petroleum thinners but a lower solvency than the high-solvency petroleum thinners and the coal tar solvents.

Turpentine is a good solvent for most of the varnish resins. It will not dissolve the fossil and some phenolic resins, however, but, when these resins are processed with oils, the resulting oleoresinous gel is readily dissolved with turpentine. Turpentine is a very good solvent for exterior paints and is used extensively by painters.

Turpentine will dissolve the long-oil alkyd resins, but some coal tar solvents must be admixed with turpentine for it to be used as a thinner for short-oil alkyds.

Turpentine may be used in limited quantities in lacquers.

**Petroleum Thinners.\*** They were commercialized in 1854 and were first introduced in the varnish industry around 1885, when Samuel Banner, of Liverpool, obtained a patent on "a new or improved substitute for turpentine." The petroleum thinners were originally considered an inferior substitute for turpentine, but better understanding of their properties and uses soon established them as vital factors in the varnish industry.

By admixing various fractions of petroleum distillates, petroleum thinners of many practical evaporation rates and distillation ranges can be obtained.

\* Petroleum solvents have been generally called "thinners."

The common petroleum thinners are pentane, rubber solvent, gasoline, varnish and paint makers' naphtha (V.M.P. naphtha), benzine, mineral spirits or white spirits, and kerosene.

**High-Solvency Type Petroleum Thinners.** With the advent of such synthetics as phenolic resins and alkyds, there was a need for high-solvency thinners in order to obtain complete solubility, especially for the short-oil varnishes. There were a great many high-solvency thinners available, but they were rather high in price. From hydrogenated petroleums and from selected petroleums with high aromatic content, the petroleum industry provided three high-solvency petroleum thinners with distillation ranges and flash points similar to toluene, mineral spirits, and kerosene.

The continual growth of the number and diversity of synthetic products and the new uses of varnishes and enamels have necessitated the use of these new thinners, either as one of the main constituents of the total thinners or in admixtures with other thinners to get desirable properties such as high solvency, free flowing, and anti-skinning.

**Coal Tar Solvents.** This group has found extensive use in the paint, varnish, and lacquer industry. The nitrocellulose industry uses them as diluents; the ethylcellulose industry uses them in almost all formulation. They are used with polymerized styrol, wire enamels, short-oil phenolic varnishes, urea resins, melamine resins, chlorinated rubber, and a great many other synthetic resins, either as diluents or straight solvents. The more common coal tar solvents used are benzol, toluene, xylol, solvent naphtha, and high flash naphtha.

**Hydrogenated Solvents.** Hydrogenated thinners or solvents, such as cyclohexane, methylcyclohexane, cyclohexanol, methylcyclohexanol, cyclohexanone, tetrahydronaphthalene, decahydronaphthalene, and methylcyclohexanone are used to some extent in Europe and are being employed in greater quantities in the United States. Their chief drawback is high price. Their principal use, at present, is in small quantities in synthetic varnishes to decrease viscosity, increase compatibility between constituents, give good leveling, and flowing properties.

**The Esters.** These solvents have found extensive use in the lacquer industry and they are of value in the newer synthetic vehicles. Various esters find use as a common solvent for relatively non-compatible constituents such as vegetable oils (linseed) with chlorinated rubber. Among the widely used esters are ethyl acetate, butyl acetate, amyl acetate, butyl lactate, isopropylacetate, ethyl butyrate, methyl Cello-solve acetate, and Cellosolve acetate.

**Ketones.** These have been used mainly as solvents for the cellulose acetates. Newer ketones for use in varnish formulations have appeared in commercial quantities and at commercial prices. The vinyl resins (see Chapter 17, Volume I) of the copolymer type have created a demand for ketones. Many resins can be used in varnishes because of the relatively low-priced ketones. Some of the widely used ketones are acetone, methyl acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl amyl ketone, methyl propyl, and methyl butyl ketone.

**Ethers.** The ethers of the higher boiling series are used in lacquers and with some synthetics. Among those used are dichloroethyl ether, diethyl Cellosolve, and diethyl carbinol.

**Chlorinated Solvents.** These solvents are employed in the varnish industry because of their high solvency. They have been used with a great many synthetics which are insoluble in other solvents. The polyvinyl chlorides are put into usable form by employing these solvents. Among those used are amyl chloride, monochlorobenzene, monochlorotoluene, tetrachloroethane, ethylene dichloride, and trichloroethane.

**Alcohols.** This class of solvent has been used to a large extent by the varnish industry in spirit varnishes, which derived their name from the alcohol spirits. The newer synthetics such as the vinyls, ethylcellulose, and others use denatured alcohol as a solvent. The higher alcohols, such as butyl, have become very important as a solvent for alkyds, urea, and melamines; they are also used as solvents during resin formation.

**Alcohol Ethers.** These solvents, especially the Cellosolves, have found extensive use in the lacquer industry. They are now finding place in synthetic varnishes as a common solvent for the various constituents in a varnish and also to increase the amount of diluents in a formulation to decrease cost.

## CONSTITUENTS USED IN SMALLER AMOUNTS

The constituents we have just discussed are used in large quantities in varnish making. Besides these, there are others—anti-skinning agents, flattening agents, plasticizers, waxes, mineral oils, and greases—which are used in small quantities to impart specific properties to varnishes.

### Anti-Skinning Agents

The early development of the quick-drying varnishes were attended with difficulties connected with the tendency of these varnishes to change consistency on storage and to gel and skin on standing in the container or particularly when exposed to the air. Overcoming these difficulties by careful formulation and processing without the use of outside ingredient is preferable and is successfully accomplished with many varnishes. To meet rigid specifications, it is sometimes necessary to use outside ingredients, usually called antioxidants and anti-skinning agents. There are two general types of anti-skinning agents: (1) the antioxidant type, of which the polyhydroxy phenols and their derivatives are the most efficient, and (2) the solvent type. The latter type prevents skinning in two ways: by acting as a dispersant (solvent) for highly polymerized products and so keeping the gelled particles from coalescing to a continuous film (skin); and by having the ability to absorb oxygen readily without altering its volatility in the process. A list of anti-skinning agents is given in the *Scientific Section Circular 400*, National Paint, Varnish and Lacquer Association, Washington, D. C., 1935. This circular also describes tests conducted on the materials. The edible oil chemists have shown that vegetable lecithin is a material having antioxidant properties when used in vegetable oils where autoxidation is catalyzed by an active metal.

### Flatting Agents

Dull clear varnishes are very popular because of the very restful psychological effect of this type finish. The dull effect is obtained by dispersing a large number of microscopic particles throughout the vehicle to diffuse the reflected light. Many materials are used to produce this effect. They are waxes, gums, diatomaceous earth, magnesium carbonate, and zinc and aluminum stearates. This effect can also be obtained by incompatible mixtures.

For a detailed discussion, see Chapters 18 and 27, and the section on magnesium carbonate in Chapter 17, all in Volume II.

**Zinc Stearate.** Two to 6 per cent of the zinc stearate, based on the non-volatile content of the vehicle, is recommended for use. First a soft creamy paste is made by dispersing 20 parts (by weight) of zinc stearate in 80 parts of mineral spirits by means of heat at 140–160° F. (60–71.1° C.). This paste is added to varnishes simply by stirring or by mixing and passing through the roller mill once.

**Aluminum Stearate.** This is used as a flattening agent by taking advantage of the fact that it will not dissolve or form gels below its gelling temperature. This demands that the aluminum stearate be dispersed in the vehicle in a pebble mill to avoid the excessive heat developed by grinding with other types of mills. Depending upon the vehicle and its solvent or thinners, 5 to 20 per cent is used.

### Plasticizers

**Definition \* of Plasticizers.** "A plasticizer is a liquid or solid material added to plastic or semi-plastic compositions to increase the permanent flexibility. Through common usage, the term has been extended beyond its strict interpretation and is generally considered to cover the imparting of such qualities or combinations of qualities as elasticity, flow, distensibility, gloss, clarity, adhesion, resistance to water, solvents, and reduction of burning rate."

**Properties of Plasticizer.** An ideal plasticizer should be:

- |                     |                                 |
|---------------------|---------------------------------|
| 1. Odorless.        | 6. Non-inflammable.             |
| 2. Colorless.       | 7. Stable under heat and cold.  |
| 3. Tasteless.       | 8. Non-yellowing.               |
| 4. Non-toxic.       | 9. Compatible.                  |
| 5. Non-hygroscopic. | 10. Inert to reactive pigments. |

It should have:

- |                              |                           |
|------------------------------|---------------------------|
| 1. High flash point.         | 4. High solvent strength. |
| 2. High boiling range.       | 5. Low solvent retention. |
| 3. Low vapor pressure.       | 6. Dispersing power.      |
| 7. Wettability for pigments. |                           |

It should impart:

1. Gelatinizing power with nitrocellulose.
2. Free-flowing properties with fast-setting resins.
3. Stability to consistency on aging.
4. Distensibility to permit flow under stress without rupture.
5. Distensibility without too great a loss in tensile strength.
6. Toughness to varnish film to withstand impact.
7. Permanent flexibility and toughness to film on aging to avoid crumbling, stickiness, greasiness, and brittleness.

It should enable the film to elongate and contract during temperature change and stay within the practical elastic limit.

\* By Arnold Kirkpatrick, Plasticizer Section, Monsanto Chemical Co.



It should control shrinkage during film formation to avoid pores and maintain a solid continuous film; and it should control shrinkage to increase the adhesion by reducing internal stresses within the film and enable the adhesion constituent of film to work freely.

Naturally, no one plasticizer or combination of plasticizers possesses these properties in their entirety, but the greater the number of these properties that are included in a plasticizer or a combination of plasticizers, the greater the scope of the varnish. In preparing a varnish for a particular specification, a great many of these properties are not necessary, but as a rule are not harmful if the film possesses them.

Some of the more important plasticizers are given in the chapter on lacquer solvent, Chapter 27, Volume I.

### **Wax, Mineral Oils, and Greases**

**Waxes.** Such waxes as paraffin, carnauba, and beeswax are well known to the average paint and varnish formulator and have been used for many years. Mineral oils and greases have also been used in varnishes, but mainly for specialty coatings. The broad scope of varnishes has introduced into common use a great many organic finishes, which in the past were considered specialty coatings. The greater employment of mineral oils and greases in varnishes is now a matter of common knowledge and has taken them away from the highly specialized fields.

Waxes vary in melting points and structure, from semi-gelled amorphous masses to hard amorphous and crystalline materials melting at approximately 200° F. (93.3° C.).

The waxes impart specific properties to varnish films. The amorphous waxes impart penetration and flexibility; the crystalline material imparts reduced penetration, and hardness. By blending waxes added to varnishes, varying degrees of these properties can be obtained.

**Synthetic Waxes.** These are also available. Hydrogenation of vegetable oils such as cottonseed and soybean have produced a range of wax-like materials of varying hardness and melting points. Hydrogenation of fish oils has also produced a series of wax-like materials of different degrees of hardness and melting points, supplying a fairly complete range from which to choose.

Chemical treatment of phenolic compounds has also offered waxy materials of considerable merit. The chlorinated naphthalenes are an outstanding group of wax-like compounds that are finding extensive use commercially.

**Mineral Oils.** They are discussed in detail in the section on mineral oils, Chapter 21.

**Wax Tailings, Petroleum Greases, Heavy Tarry-Like Flux Oils.** They have been used for years in compounds and waterproof baking coatings. The waterproof baking coatings are, as a rule, long- and short-oil asphaltic varnishes. Within the last three to five years, heavy lubricating oils, refined mineral oils, paraffin oils, etc., have been used quite extensively alone or together with waxes in synthetic baking varnishes to impart characteristics inherent in these materials. They impart to varnishes increased waterproofness, antioxidant properties, flexibility, heat resistance, and special surface finishes, such as temporary adhesion.

Heavy mineral oil and grease combination will give a greasy finish on coated fabrics that will enable stacking without slipping. By adjusting the amounts of grease and mineral oil, a slip property can be imparted to the dried varnish film on coated fabric. This will enable the coated fabric to slide easily for application purpose. Wax added to some flexible varnishes will enable the coated fabric to be stacked or rolled tightly without offsetting on aging.

Satin frosting and similar finishes may be obtained by regulating wax and grease mixture of a varnish.

## VARNISH FORMULATION AND PROCESSING

### Natural Varnishes

These varnishes are obtained by tapping the varnish tree (Tsi-chon) indigenous to China and Japan. The resulting liquid saps are thick, milky emulsions which have the rather unusual properties of drying only in a moist atmosphere. The dried natural varnish films are exceedingly hard and durable and possess excellent resistance to water. These varnishes are used largely by the Chinese and Japanese in executing the beautiful lacquer work for which they are famous.

### Processing Natural Resin Varnishes

Natural hard resins, such as congo, kauri, manila, and others, in their native state, are insoluble in linseed and other drying oils. It is necessary first to decompose and depolymerize the resin by heating, above its softening point, to temperatures from 600 to 670° F. (315.6–354.4° C.). During this period, there is a loss in weight of the resin

of 15 to 35 per cent, depending upon the original hardness of the natural resin. At the end of this depolymerization period the oil, either in the raw or bodied state, is added; and then heat processing is continued until the mixture of oil and resins has completely reacted and has been bodied to the desired viscosity. Then the processed material is cooled and driers and thinners are added on the down heat, in the order named at temperatures not higher than 400° F. (204.4° C.).

This preheating of the natural resins to insure compatibility or solubility with the vegetable oils is generally called the "melting" or "cracking" process. The natural resins have greatly different melting points and thus must be treated differently. For specific details, see Chapter 8, Volume I.

During the melting period, many of the properties of the natural resins are either improved or destroyed by the heat treatment employed. Heating natural resins too rapidly will often cause charring, which discolors the resulting varnish to a large extent. Rapid application of heat to the resin in the fluxing or initial stages of melting may cause flashes or fires. Lengthy periods of heat will cause extraordinary losses and usually result in a shortness or brittleness of the ultimate varnish film.

The methods of melting natural resins are described generally in two terms—"slack melting" or "fine (or close) melting."

**"Slack Melts."** Sometimes it is necessary only to heat-treat or melt the resin just enough to be barely soluble in oil. This type of melt is recognized as "slack melting" and is used to maintain pale color and to get greater viscosities in the finished varnish. There are some partially melted pieces of resins called "floaters" or "sponges" which will be suspended in the finished varnish and therefore must be removed by filtering.

Slack melts are usually made in uncovered kettles at a temperature seldom exceeding 625° F. (329.5° C.). The beginner should not at first try to slack-melt natural resins, as the result may prove discouraging owing to lack of experience.

Whereas in slack melts the kettle is usually uncovered, in "fine" or "close melting" the kettle is covered during processing.

**"Fine" or "Close Melting."** Natural resins, melted to the point of complete solubility or compatibility, are said to be fine or close melts. This is the method generally used:

*Practical processing on commercial scale:*

1. In a clean portable copper varnish kettle are put upwards of 150 pounds of solid resin.

2. The kettle is then placed directly over a fire pit and heat is applied slowly so that in 10 minutes a temperature of 350° F. (168.3° C.) is reached; at this temperature the resin begins to melt.

3. Heat is then applied more slowly, until a thin film or layer of melted resin covers the bottom of the kettle, protecting from charring the remaining unmelted resin.

4. From this point, the temperature is permitted to rise more rapidly, but great care is exercised to prevent the flames and sparks from igniting the fumes and other inflammable vapors which are given off at this time. Water vapor is also given off.

5. By the time the temperature of approximately 500° F. (260.0° C.) is reached, the resin is completely melted.

The complete melting of resin takes 25 to 30 minutes.

6. The temperature is allowed to rise to 600° F. (315.6° C.) and the kettle is removed from the fire pit, cooled for a very short time—usually 3 to 5 minutes—and then placed back on the fire pit. The temperature is then raised to 635° F. (335° C.). At this point, the temperature rises spontaneously about 20° F., and at this heat the melted resin is processed for about 8 to 10 minutes.

7. This cooling, reheating, and processing are repeated a second time with most resins. With resins of increased hardness, a third and fourth cooling and reheating may be necessary.

An examination of the melted resin should show that it is a homogenous liquid, free of strings or sponginess.

The cooling period is known as the "sweating" period. During this time the solid portion of resin approaches the liquid state without the further application of heat.

8. Now the temperature is allowed to drop slightly, a given amount of heated oil is added to the melted resin, and the mixture is further heat-processed until the resin is completely dispersed, dissolved, or reacted with the oil.

The "end point" of this reaction is reached when a clear bead is obtained on cooling a drop of the homogenous (mixture) fluid on a glass. If the reaction is still incomplete, the bead will be cloudy.

The end point becomes evident as the drip from a paddle develops to a continuous string, varying in length from 8 inches upward. While the resin is still not completely dispersed or reacted with the oil, the drip will be discontinuous, and the unmelted resin can be easily discerned in the flowing drip.

9. The combined oil and resin are then allowed to cool, driers are added, and the whole is reduced with thinner—usually at temperatures of 350–375° F. (168.3–189.6° C.).

A "heat" is that period during which the melted resin is cooled—usually 3 minutes—reheated to top temperature—requiring about 3 minutes—and then processed at top temperature for about 5 to 6 minutes.

Two heats are generally sufficient for fine melting; the covered kettle allows higher temperature to be reached with considerably more safety than the open kettle. Three and sometimes four heats are necessary when resins form solid masses, owing to excessive initial heat. This may be avoided, either by gentle application of initial heat or by the use of a small amount of rosin to act as a flux.

Fine melt resin may be made in many ways, and there is not complete agreement on the best method to use. Perhaps a fine melt should be defined according to the properties of the processed resin rather than the heating method employed. A fine melt resin, therefore, would be one which dissolves very easily in oil.

Because much higher temperatures are reached in closed kettle melting, it is essential that the preheated oil be added as soon as the temperature has receded 15 or 20 degrees from the peak. This procedure will eliminate any marked degree of resin discoloration and will keep the losses within an efficient operating cost range. After the oil has been added, the cover is removed and the batch treated as described in "fine" melting.

In closed kettle melting, a certain amount of distillate will condense in the well or sunken portion of the cover. A considerable quantity of distillate is developed at the end of the first heat. Care must be exercised when removing the kettle from the fire pit to avoid spilling or splashing any of this condensate because it is inflammable. It is removed from the cover with pieces of burlap, by carefully wiping or mopping toward the front of the kettle. The burlap is usually disposed of by burning at the end of the day's run.

It should be mentioned that if an operator is careless in the melting of resins, flashes or fires may occur. With reasonable care and strict attention to the job, years pass without a fire occurring. If, however, there is one, it is easily extinguished either by the application of water directly into and on the outside of the kettle or by the application of chemical fire extinguishers. When water is used to extinguish fire, replace the melting kettle on the fire pit, hold at a low temperature to expel the water, and then apply the usual heat treatment. This procedure works only when the fire has occurred while melting the resin, and not after the addition of oil.

**"Oil Melts."** In this processing, the resin is added directly to the cold oil and both are heated to the temperature necessary to get dispersion or solubility. Kauri seed and chips, east india, and dammar are commonly used in oil melts.

## Laboratory \* "Running" or "Processing" of Natural Resins and Processing of Natural Resin Varnishes

For the beginner, here is given practical laboratory data on the "running" or "processing" of the natural resins, such as congo and kauri, and the making of natural resin varnishes, with these resins and batu. The data are shown graphically in Figs. 1-7.

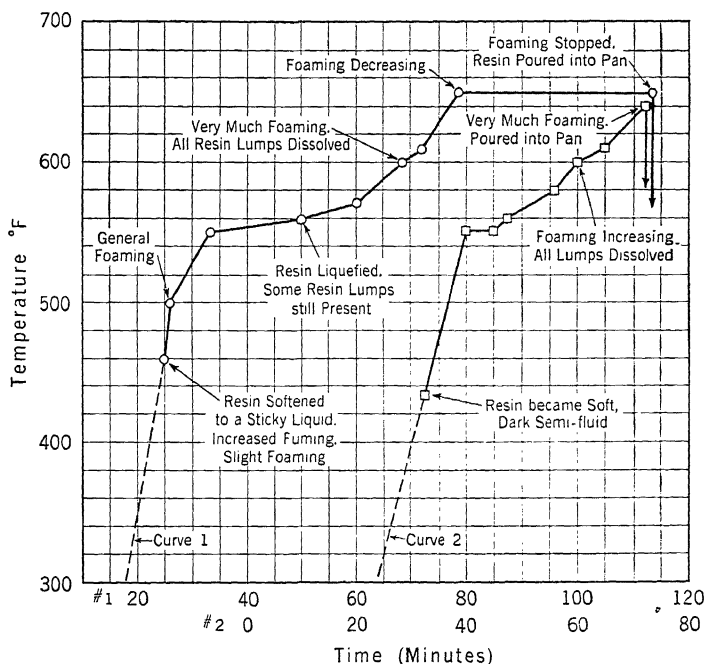


Fig. 1. Typical Time-Temperature Charts. Processing Congo (Laboratory Batches).

Curve 1 (O) = "fine melt" congo; curve 2 (□) = "medium melt" congo.

**Congo—"Running" or "Processing." Fine Melt.** In Fig. 1, curve 1, is shown the running of congo to a fine melt. Place 500 grams of congo in a 1,500-cc. glass beaker and heat to a temperature of 650-670° F. (343.3-354.4° C.), taking about 1¼ to 1½ hours to reach this temperature. Hold batch at this top temperature about one-half hour, i.e., until all foaming subsides and the resin drips like hot oil from a paddle. If a clear bead is obtained from a drop of oil poured on glass, then the congo will readily incorporate with drying oils. The loss in processing is 33 per cent.

\* Submitted by Charles Ferri and Anthony Skett of the American Gum Importers Association.

*Medium Melt.* In Fig. 1, curve 2, is shown the running of congo to a medium melt. Here also 500 grams of congo is processed, but the top temperature is 640° F. (337.8° C.). The loss in processing here is 23 per cent.

**Congo-Tung and Linseed Oil Varnishes.** *Run Congo Varnishes.* In Fig. 2 is shown graphically the laboratory processing of tung oil and linseed oil varnish with "runned" or "processed" Congo resins. Curve 1A illustrates the making of

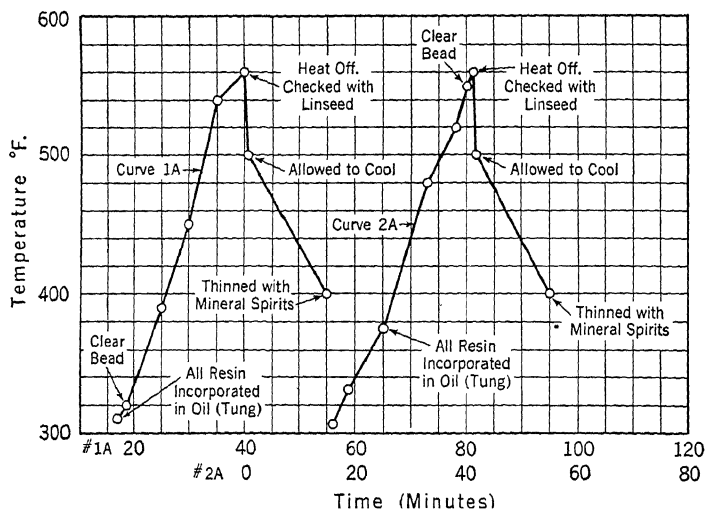


FIG. 2. Typical Time-Temperature Charts. Congo-Tung-Linseed (Processed Congo) Varnishes.

Curve 1A = "fine melt" congo; curve 2A = "medium melt" congo (laboratory batches).

the varnish using the fine melt congo; curve 2A illustrates that of the varnish using the medium melt congo.

The formula and the cooking procedure for the two varnishes are the same:

*15 gallons congo-tung and linseed oils*

- 120 grams "run" congo
- 115.5 grams tung oil
- 28.5 grams bodied linseed oil (Z viscosity—22.7 poises)
- $x$  grams drier, e.g., to 0.15% Pb, 0.05% Mn, 0.05% Co, based on the weight of the oil
- $y$  grams mineral spirit, to 70% non-volatile

*Cooking procedure:* Heat the run congo and the tung oil to 560° F. (293.3° C.) in about 40 minutes. At this point test for clear bead, and then check immediately with linseed oil. Cool to 400° F. (204.4° C.); then add drier and mineral spirits.

The percentage loss in the preparation of the varnish with the fine melt resin is approximately 1 per cent, whereas that for the medium melt resin is approximately 2 per cent.

The viscosities of the varnishes at 70, 65, 60, 55, 50, and 40 per cent non-volatile are shown graphically in Fig. 3. It is to be noted that the viscosities of the varnishes made with the fine melt resins are lower than those of the varnishes made with the medium melt resins.

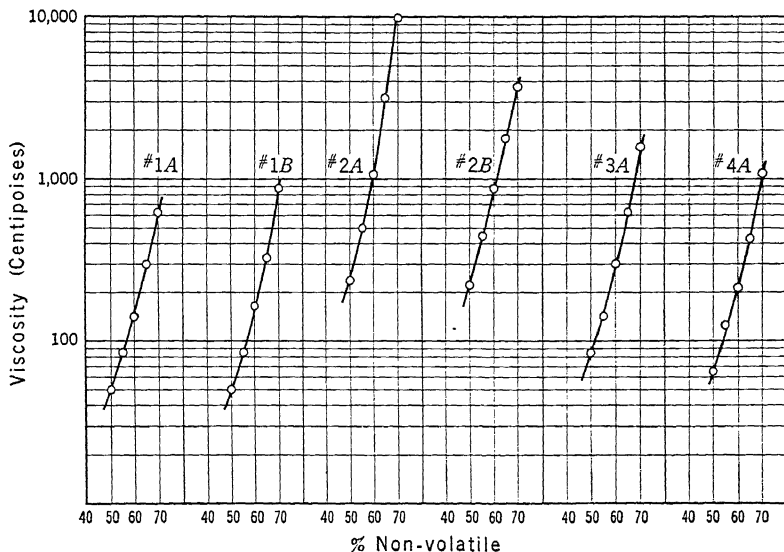


FIG. 3. Relationship between Non-volatile Content and Viscosity for Natural Resin Varnishes (15 Gallons Oil Length).

1A = "fine melt" congo, tung (80%), linseed (20%).

1B = "fine melt" congo, linseed.

2A = "medium melt" congo, tung (80%), linseed (20%).

2B = "medium melt" congo, linseed.

3A = "fine melt" kauri, linseed.

4A = batu, tung (80%), linseed (20%).

In Fig. 4 is shown graphically the laboratory processing of a linseed and run Congo resin. Curve 1B illustrates the making of the varnish using the fine melt congo; curve 2B illustrates that of the varnish using the medium melt congo.

The formulation and the processing of the two varnishes are the same:

*15 gallons run congo-linseed oil*

120 grams run congo

144 grams bodied linseed oil (Z viscosity—22.7 poises)

*x* grams drier, 0.15% Pb, 0.05% Mn, 0.05% Co, based  
on the weight of the oil

*y* grams mineral spirits, to 70% non-volatile



*Cooking procedure:* Heat the run congo and the bodied linseed oil to 580° F. (304.4° C.) in about 50 minutes. Test for clear bead. Cool to 400° F. (204.4° C.), and then add drier and mineral spirits.

The loss in processing for the fine melt resin is approximately 3 per cent, whereas that for the medium melt is approximately 3.5 per cent.

The viscosities for these varnishes at 70 to 40 per cent non-volatile are shown graphically in Fig. 3. Again it is to be noted that the varnishes made with the

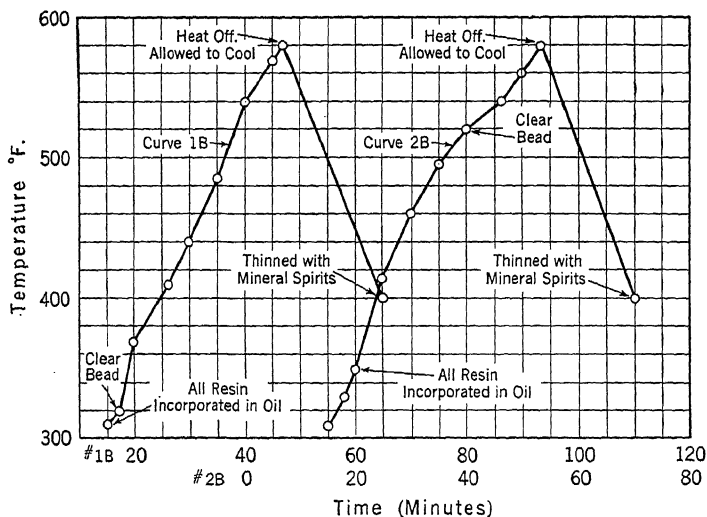


FIG. 4. Typical Time-Temperature Charts. Congo-Linseed Varnishes (Processed Congo).

Curve 1B = "fine melt" congo; curve 2B = "medium melt" congo (laboratory batches).

fine melt congo are lower in viscosity than those obtained with the medium melt congo.

**Kauri—Running.** Heat 500 grams of kauri in a 1,500-cc. beaker, taking 1¼ hours to reach 625° F. (335° C.). Hold at this temperature for one-half hour or longer, e.g., until all foaming subsides and the resin drips like a clear hot oil from the paddle. Figure 5 shows this processing graphically.

The running of the kauri may be generally described as follows: The resin first chars and softens at the bottom of the container. Then it softens to a dark brown gummy substance. As the resin continues to soften, it begins to develop slight foaming, which increases in intensity as the resin melts to a sticky mass. The foaming increases to the greatest intensity as the top temperature of 625° F. (335° C.) is approached, and here the run kauri should be a lumpy liquid. When the foaming subsides, the run kauri should flow like a clear hot oil.

The loss in the running of the kauri is approximately 30 per cent.

**Kauri-Linseed Varnish.** In Fig. 6 is shown the processing of a 15-gallon run kauri and linseed oil varnish. The formula for the varnish is:

*15 gallons kauri-linseed oil varnish*

120 grams run kauri (No. 3)

144 grams bodied linseed oil (Z viscosity—22.7 poises)

$x$  grams drier, 0.15% Pb, 0.05% Co, 0.05% Mn, based  
on the weight of the oil

$y$  grams mineral spirits, to 70% non-volatile

*Cooking procedure:* The processing of this varnish is the same as that given for the congo-linseed varnish described on page 220.

The loss in processing is approximately 2.6 per cent.

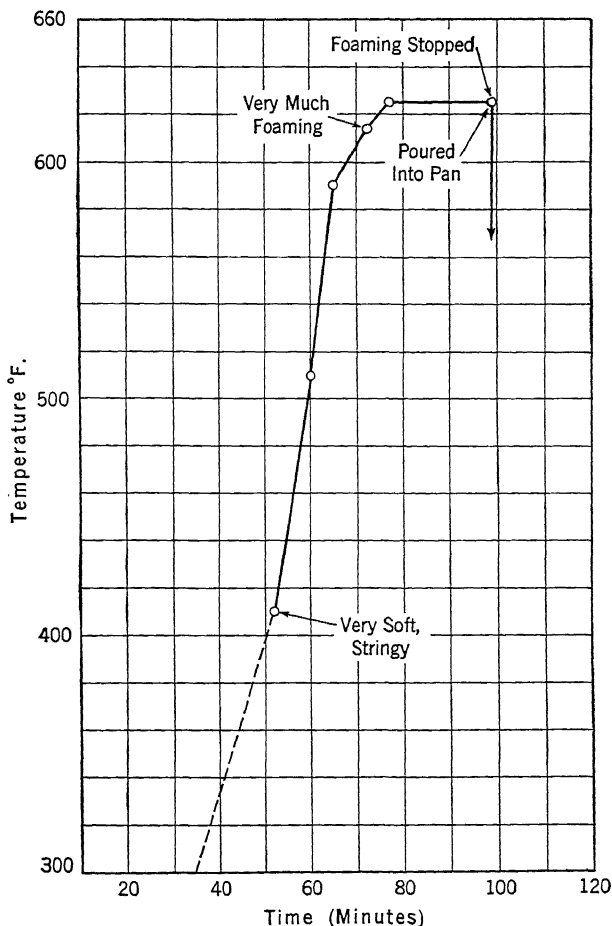


FIG. 5. Typical Time-Temperature Chart. Processing Kauri to "Fine Melt" (Laboratory Batch).

The viscosities of this varnish at 70, 65, 60, 55, and 50 per cent non-volatile are shown graphically by curve 3A in Fig. 2.

**Batu-Resin Varnish.** Batu resin does not have to be runned or processed prior to its use in making varnish. In Fig. 7 is shown the processing of 15 gallons

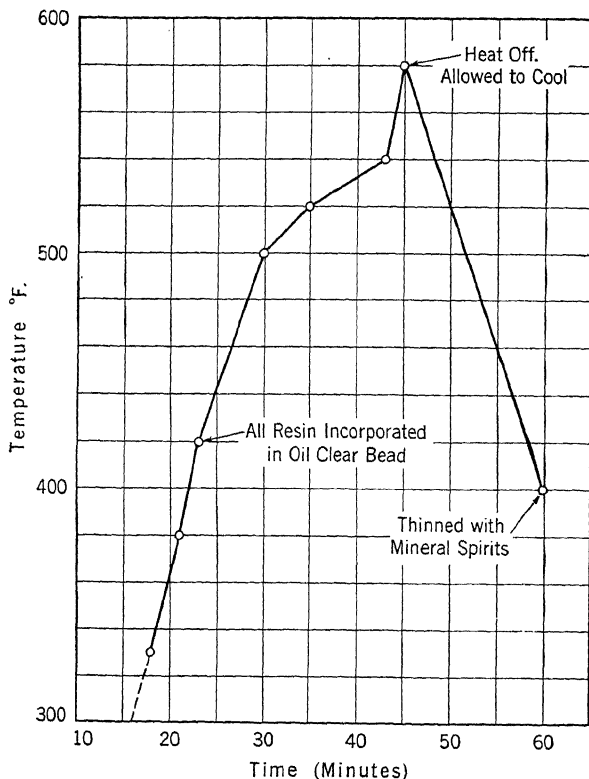


FIG. 6. Typical Time-Temperature Chart. Kauri-Linseed Varnish No. 3; Processed Kauri (Laboratory Batch).

of batu-tung and linseed oil varnish. The formula and the cooking procedure are as follows:

*15 gallons batu-tung and linseed oil varnish*

160 grams batu, scraped

154 grams tung oil

38 grams bodied linseed oil (Z viscosity—22.7 poises)

$x$  grams drier, 0.15% Pb, 0.05% Mn, 0.05% Co, based  
on the weight of the oil

$y$  grams mineral spirits, to 70% non-volatile

*Cooking procedure:* Heat batu and 80 grams of tung oil to 620° F. (326.7° C) in 1 to 1¼ hours. Test for clear bead. Cool to 540° F. (282.2° C.) and then

add the remainder of the tung oil (74 grams). When the temperature drops to about 460° F. (237.8° C.), reheat quickly to 540° F. (282.2° C.). Check immediately with the 38 grams of linseed oil. Cool to 400° F. (204.4° C.) and add drier and mineral spirits.

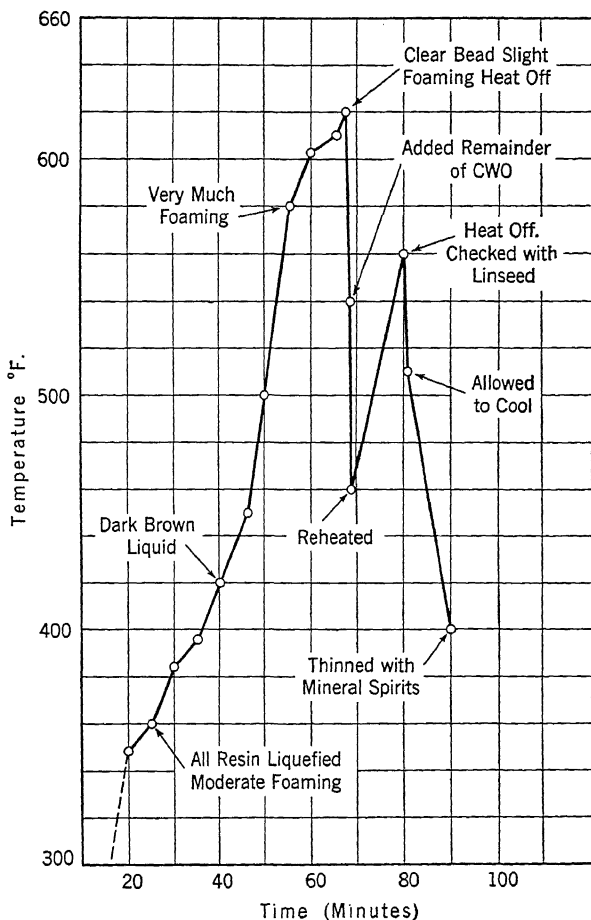


Fig. 7. Typical Time-Temperature Chart. Batu-Tung-Linseed Varnish No. (Laboratory Batch).

The loss in processing the varnish is approximately 7 per cent.

The viscosities of the varnish at 70, 65, 60, 55, and 50 per cent are shown graphically by curve 4A in Fig. 2.

**General Remarks.** These results can be generalized as follows:

1. The finer the melt, the greater the loss during the running or processing. The average loss during running of congo or kauri on small laboratory batches

is about 30 per cent to 35 per cent for a fine melt and 20 per cent to 25 per cent for a medium melt.

2. The ease of compatibility of drying oils with run Congo or kauri resin varies proportionally with the amount of running that the resin has undergone.

3. All other factors being equal, the longer the running of congo or kauri, the lower will be the viscosities of the varnishes made with them. It might be pointed out that, if high viscosities are desired with these two resins, they should be pre-processed to a medium or slack melt before incorporation with oil.

4. Batu resin does not require processing prior to its use for manufacturing varnishes.

*Conclusion.* It is interesting to note that in general the running of the natural resins and the making of these varnishes are equally applicable to large-scale production. If the rate of increase to top processing temperature, time of holding the material at this temperature, and the rate of cooling are held close to the same conditions as in the laboratory, then the results in the laboratory can be duplicated reasonably well in factory production scale.

**Zanzibar Resin.** This is an exceptionally hard, pale, transparent natural resin which is difficult to "melt." Owing to its hardness, it requires exceptionally high temperatures and expert handling to preserve its pale color. In previous years this resin was used as a basis for spar, floor, and carriage varnishes and also for piano and first-class furniture finishing. Varnishes could be made with this resin which would be pale in color, have high gloss, hard surface and give good polishing properties.

**Kauri Resin.** Varnishes produced from kauri resin are usually quite dark, except of course those made from the premium grade, such as "five cross," which is generally marked xxxxx.

The processing of a No. 2 brown kauri bold resin varnish is presented graphically in Fig. 8. To avoid excessive darkening of the dark kauri, a small amount of rosin is often used as a flux; it is placed in the bottom of the kettle before the kauri is added. Rosin having a much lower melting point liquefies first and spreads on the bottom of the kettle, thus protecting the unmelted kauri from coming in direct contact with the hot metal of the bottom of the kettle. The heat is then applied slowly and the temperature is permitted to rise at a constant rate at first, and more slowly as the first heat peak is being approached. The first cooling or "sweating" period is noted at *C* to *D*, followed with a rapid temperature rise to a second peak at *E*. Now the batch is again allowed to "sweat"—*E* to *F*—before adding preheated tung oil; there is then an immediate cooling to *G*. The kettle is placed over the fire pit to reheat the batch to *H*, in order to "cure" \* the tung oil, and at the same time incorporate it thoroughly

\* Destroy the wrinkling tendency of the tung oil.

with the melted resin. At this point, the batch is "checked" or cooled rapidly with a small amount of cold linseed oil and subsequently the drier is added. The batch is allowed to cool further and at a temperature of approximately 350° F. (176.7° C.) the thinners are added—in this instance, mineral spirits and dipentene.

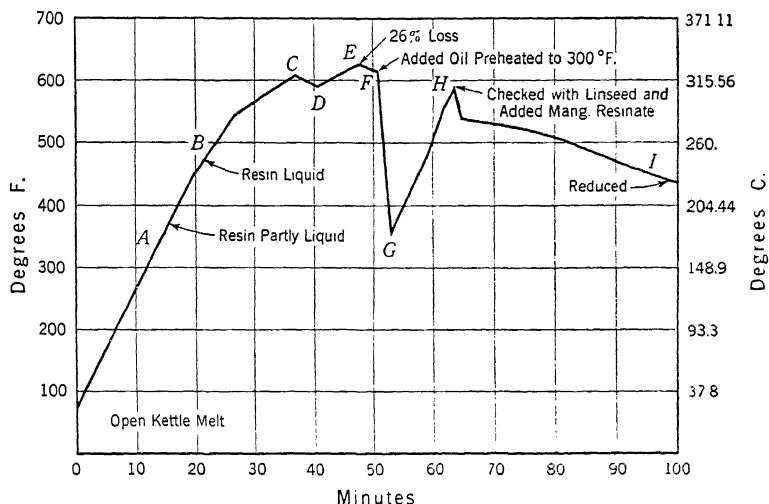


FIG. 8. Processing of No. 2 Brown Kauri Bold Resin Varnish.

- 100 lb. No. 2 brown kauri bold.
- 10 lb. F rosin.
- 11 gal. tung oil.
- 7 gal. linseed oil—body Q (4.35 poises).
- $\frac{3}{4}$  lb. manganese resinate precipitate.
- 25 gal. mineral spirits.
- 7 gal. dipentene.

Speed is essential in melting all grades of kauri; the shorter the melting period, the paler the color of the finished varnish. The procedure just described may be used on all grades of kauri except, of course, the dust and chips. These are usually used in oil melts or with large amounts of rosin; here much lower temperatures are necessary to insure oil solubility.

**Congo Resin.** The processing of opaque Congo and No. 2 Congo varnishes are shown graphically in Figs. 9 and 10, respectively. The processing of a spirit varnish, Pontianak bold resin and solvent, is shown in Fig. 11. This latter varnish is usually used for cold cuts in vehicle mixtures.

### Rosins, Varnishes

The simplest varnishes are those produced by dissolving or dispersing resin in volatile thinner, such as rosin dissolved in mineral spirits or other solvents.

The dried film obtained from such a varnish is brittle and can be easily powdered by simply rubbing with the finger. Such a film ex-

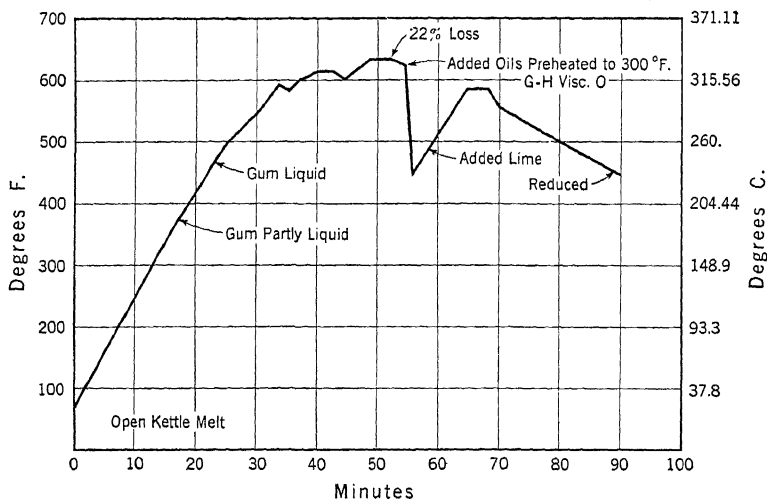


Fig. 9. Processing of Opaque Congo Varnish.

- 100 lb. opaque congo.
- 15 lb. W. W. rosin.
- 4¼ gal. tung oil.
- 4½ gal. varnish-grade linseed oil.
- 4 oz. lime.
- 23 gal. mineral spirits.

posed to air gradually crumbles because of oxidation. In addition, owing to the high acidity of rosin, it cannot be used with basic pigments, because "livering" will result. (See Volume IV.) A rosin solution varnish is usually unstable, as the rosin may separate in crystalline form on aging in storage.

These defects can be partly eliminated by neutralizing the acidity of the rosin with a base such as lime (calcium hydrate) or zinc oxide, or by combining with glycerol, thus forming "ester gum." (See Chapter 10, Volume I.)

When lime is employed to neutralize the rosin, the resulting product is known as "lime-hardened rosin," and the method is generally

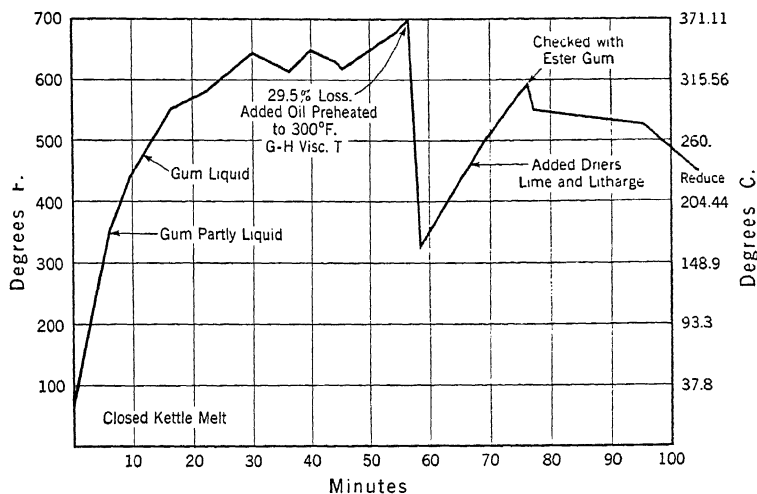


FIG. 10. Processing of No. 2 Congo Varnish.

125 lb. No. 2 congo.  
 17¼ gal. tung oil.  
 4 gal. linseed oil—body Q (435 poises).  
 2 lb. litharge.  
 1 lb. lime.  
 25 lb. ester gum.  
 37½ gal. mineral spirits.

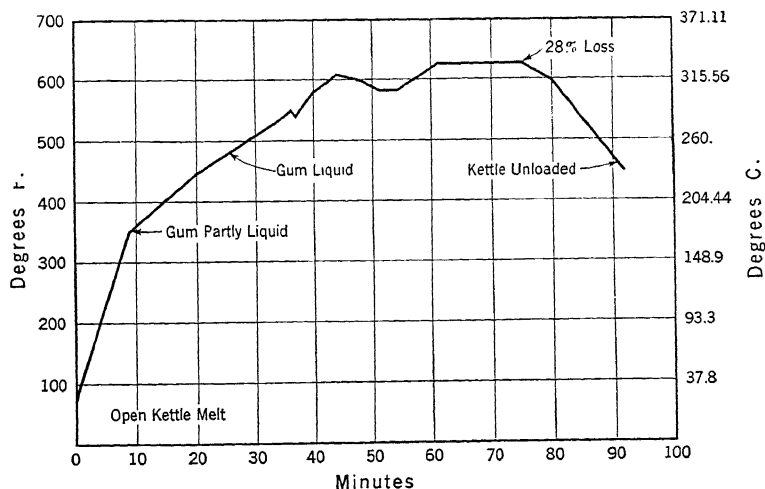


FIG. 11. Processing of Spirit Varnish Pontianak Bold Resin and Solvent.



known as "liming." This is usually effected by first melting the rosin, then heating to 450° F. (232.2° C.), and slowly sifting into it finely powdered lime while constantly stirring; then raising the temperature to 525° F. (274.4° C.) and holding it at this temperature until the reaction is completed. The temperature of the batch is then permitted to drop to approximately 350° F. (176.7° C.) and it is thinned with mineral spirits. This varnish is known as a "gloss oil."

In the formulation of a varnish, we begin with 100 pounds of rosin (acid number approximately 163), and for this amount 8.77 pounds of lime are needed for complete neutralization. The calcium resinate so produced is not fluid at normal room temperatures. It is also insoluble in mineral spirits. It is necessary to leave a portion of the rosin unneutralized to dissolve the calcium resinate in mineral spirits. The acid number of rosin must not be reduced lower than 65 to 70 to obtain good dispersion of limed rosin in mineral spirits.

Common practice has shown that 6½ to 7 pounds of lime to 100 pounds of rosin are generally needed to produce a satisfactory "gloss oil." If rosin is limed in presence of oil, a maximum of 8 per cent lime is used. It is important that the lime (calcium hydrate) be free from moisture as water causes crystallization and free from magnesia which gives insoluble soaps.

In general, liming rosin increases its melting point, decreases the free abietic acid, i.e., reduces the acid number, and decreases the tendency of the rosin to crystallize.

Often a mixture of lime and zinc oxide is used to harden rosin. Here is a very short-oil (2-gallon) lime and zinc oxide hardened varnish:

#### TWO-GALLON HARDENED VARNISH

100	lb.	Gum rosin
2½	lb.	Lime
3¼	lb.	Zinc oxide
2	gal.	Bodied (40 poises) linseed oil
2½	gal.	Mineral spirits
8	gal.	Benzine

gal. Approximate yield

**Cooking or Processing Procedure.** Melt rosin to 390° F. (198.9° C.). Permit temperature to rise to 450° F. (232.2° C.) and add zinc oxide, then lime, stirring constantly until reaction ceases. Raise temperature to 575° F. (301.5° C.) and add one gallon of linseed oil. When temperature drops, raise again to 575° F. (301.5° C.)

and add another gallon of linseed oil. Hold till clear pill is obtained. Cool to 480° F. (248.9° C.) and reduce with mineral spirits, then with benzene.

**Uses.** This varnish is used as a bronze liquid, to shorten the oil length of the longer oil varnish and to impart luster to general-utility enamels. It is used also in cheap enamel vehicles.

### Ester Gum, Varnish

#### 30-GALLON ESTER GUM VARNISH

100 lb. Ester gum  
30 gal. Raw tung oil  
1½ oz. Sulfur  
60 gal. Mineral spirits  
¾ gal. Cobalt drier, 3%

100 gal. Approximate yield

**Cooking Procedure.** Heat ester gum and 30 gallons of tung oil to 500° F. (260.0° C.). Hold at this temperature for string. Cool and, at 480° F. (248.9° C.), reduce with mineral spirits and add driers.

**Uses.** Before the advent of phenolic synthetic resins, this varnish was used as a spar varnish and for general exterior purposes. It is used in making enamels.

### Cumar Varnishes

**Insulating Varnish.** This varnish can be used as a clear baking varnish for impregnating coils, etc., to impart specific electric properties and specific physical characteristics. The influence of the cumar resin in this combination gives penetrating properties, high gum content with flexibility, an amorphous structure to high gum varnish, increasing toughness, binding strength, and good cohesion and adhesion.

*Formula:* 10 gal. tung oil  
20 gal. linseed oil  
10 gal. perilla oil  
70 lb. cumar resin (V2 grade)  
30 lb. modified phenolic  
3 lb. manganese drier (6% metal)  
6 lb. lead drier (16% metal)  
45 gal. gasoline

Heat 5 gallons of linseed oil and 50 pounds of cumar resin to 600° F. (315.6° C.) and hold at this temperature for one-half hour. Then add tung oil and heat to 560° F. (293.3° C.), drop temperature to

450° F. (232.2° C.) and hold at this temperature for 2 hours. Add 20 pounds of cumar and 30 pounds of modified phenolic resin and reheat to 470° F. (243.3° C.). Hold at this temperature for 2 hours; then add 15 gallons of bodied linseed oil and 10 gallons of bodied perilla oil; reheat to 500° F. (260° C.) and hold one hour at 460° F. (237.8° C.) (Viscosity—Body G-H \*—[1.65–2.00 poises]). Cool, thin, and add driers.

### Bituminous Varnishes

Bituminous substances, such as liquid asphalt (natural), coal tar and petroleum pitches, gilsonite and manjak pitches, are important raw materials of the paint and varnish industry. These materials are discussed in greater detail in Chapter 28, Volume I.

The natural liquid asphalt, petroleum, and vegetable pitches are used after proper processing to produce paint vehicles and as blending vehicles to impart elasticity to the harder bituminous resin varnishes. With such vehicles only the dark-colored paints, such as browns, reds, or greens, can be made.

**The asphalts or pitches** are processed much the same as other resins, that is, the pitch or asphalt, either alone or mixed, is placed in the kettle and melted by means of heat, until uniformly blended. Usually temperatures from 450 to 580° F. (232.2–304.4° C.) are used. To produce flexible vehicles, vegetable oils are usually added after the asphalt or pitch, or mixtures of them, is melted. Linseed or tung oil, alone or in combination, is employed when air-drying vehicles are desired. Soybean oil, corn oil, cottonseed oil, or fish oil is added to produce heat-resisting paints, such as smokestack coatings, or aluminum liquids for hot surfaces. Coatings of this type are splendid protection for metal surfaces.

**Coal-tar pitches**, alone or in mixture with petroleum pitches, are used extensively as the base of dampproofing paints. These pitch coatings are made in heavy consistencies which are "cut back" or "reduced" with a petroleum distillate to a thin viscosity for application to cement or brick work, roofs, etc. When mineral or fibrous substances, such as clay or asbestos, are added to these vehicles, they are used as a troweling cement for either interior or exterior coatings and for foundations above and below ground. These fibrous paints are usually made in agitated steam-jacketed kettles but can also be mixed cold.

\* Gardner-Holdt Scale.

**Gilsonite and manjak pitches** are generally used for the higher quality black varnishes, which are often referred to as black japans.

The clear, unpigmented japans are solutions of bituminous material such as gilsonite cooked with one or more of the vegetable oils. Linseed and tung oil, with or without driers, produce excellent japans. The semi- or non-drying oils, such as corn, cottonseed, and soybean, are used to produce tough, elastic films. They can be plasticized with such softer bituminous substances as petroleum residue or fatty acid pitches.

Japans are ordinarily baked at elevated temperatures to produce hard, glossy, durable, and abrasive resistant films. Higher temperature and longer time are required to get hard films when the semi- or non-drying oils are used in japans. Additional drier may also be necessary to get hard films.

The color of a high-grade clear (unpigmented) japan, when examined with transmitted light, should be brownish black and rather transparent. Carbon black or lampblack pastes are sometimes added to clear japans to increase opacity. The following is a typical japan formula and method of processing:

- 60 gal. Varnish makers' linseed oil  
(acid value 2 to 4)
- 200 lb. Gilsonite (fused)
- 75 lb. Cottonseed pitch
- 20 gal. Q (4.35 poises) bodied linseed oil
- 50 gal. Mineral spirits
- 5 gal. Distilled wood turpentine
- 10 gal. Kerosene oil

*Processing Method.* Heat varnish makers' linseed oil to 600° F. (315.6° C.). Pull kettle from fire and let temperature rise to 625° F. (328.5° C.); put back on fire and hold at this temperature until a uniform fluid mass of a heavy consistency is obtained. Allow the batch to cool to 575° F. (301.7° C.); then add the fused gilsonite and cottonseed pitch and reheat to 600° F. (315.6° C.); hold until thoroughly melted and then add the bodied linseed. Cool to 400° F. (204.4° C.) and reduce with mineral spirits and turpentine.

The gilsonite used in this high-grade clear japan is fused or melted at 600°F. (315.6° C.) and held for one hour to remove volatiles.

This japan is formulated to be used as a coating for metal parts and can be applied by dipping or spraying. A hard, tough film is produced by baking at 400° F. (204.4° C.) for four hours. At lower temperature, a much longer time will be needed to produce an equally

hard film. While most japans are used on metal, some japans are used to coat wooden articles, impregnate coils, cloth, and paper, and for many other industrial purposes.

A typical japan formula for dip, spray, or tumble application of wooden articles is:

200 lb.	Cottonseed pitch
285 lb.	Gilsonite
30 lb.	Dark rosin
7 gal.	Varnish makers' linseed oil
60 gal.	Light naphtha
20 gal.	Heavy naphtha

*Processing Method.* Heat the gilsonite and cottonseed pitch slowly to 600° F. (315.6° C.) and hold until both are melted. Stir vigorously and add linseed oil, reheat to 600° F. (315.6° C.), and then allow to cool to 550° F. (287.8° C.) and add the dark rosin. Cool to 350° F. (176.7° C.) and add the light and heavy naphthas.

Japans made from tung oil generally will bake harder at a given temperature than those made from linseed oils. With the semi-drying oils, longer baking periods or higher temperatures are necessary to produce hard films.

Driers may or may not be used; this depends, of course, upon the speed of bake required. Care must be exercised when using driers, as an excess will cause wrinkling or "pitting" of the film.

Prussian (iron) blue, umber, or japanner's brown are frequently cooked in the oils to produce better color and slight increase in drying speed. Resins are also used to produce higher gloss, tougher film, increased oilproofness, and other specific characteristics desired.

### Resin Dispersions

Another form of coatings which can be considered varnishes are the resin dispersions.

**Solvent Type.** In this group are phenolic condensation products which are cured prior to dispersion in solvent and dry to a hard film by evaporation of solvent, without the necessity of any oxidation or polymerization. These resins are dispersed usually in toluol or xylol. Such resins may be modified to meet specific uses by the addition of many of the commonly employed natural and synthetic resins, nitrocellulose plasticizers, and drying and non-drying oils.

In these coatings, a drying period of five minutes, or even less, is sufficient to produce a hard film. These films are not seriously soft-

ened, blistered, or lifted by subsequent application of the same or different coatings. They may be recoated with varnishes or lacquers containing solvents as powerful as acetone and similar ketones. Owing to the nature of the constituents, the solvents are readily released, and consequently surface drying of the film is avoided and a quick, thorough drying is obtained. These coatings are used as quick-drying primers on aircraft, primer-surfacers in the automotive industry, coatings for difficult alloys, giving good adhesion, shop coats, quick-drying industrial finishes, non-penetrating coatings, and a binder in calking compounds and plastic films. They may be blended with other varnishes to speed up drying, increase hardness, cohesion, etc.

### **Water-Dispersed or Resin Emulsions.**

This class of resin (alkyd) is completely cured prior to dispersion and, consequently, like the solvent type, dry by evaporation alone.

These emulsions are stable, as a general rule, provided that, on dilution, acid and alkalis are not used in the water, and the materials are not diluted beyond 25 per cent solids. Acids cause immediate precipitation; alkalis above a pH of 9 cause a more or less rapid separation of the resin. Films from these emulsions have flexibility and toughness over a wide range of temperature, good water resistance, good grease resistance, especially in combination with starch, clarity, generally no odor or color, good adhesion, non-penetration, good gloss, good aging, and no heat sealing. They can be pigmented in the usual manner and can be blended with starch, emulsified waxes, latex, and other water emulsions to obtain specific properties. The suggested uses for water-dispersed emulsions are:

Coating for washable wallpaper.

Decorative coating for specialty papers or boards.

Protective coating for paper and board to lay surface fibers, increase scuff resistance, and increase grease and water resistance.

As a plasticizing and greaseproofing agent when used in conjunction with starch, casein, etc.

As a base coat to provide good anchorage and prevent excessive penetration of top coats.

As a sealer coat on asphalt or rubber-filled paper or fabric.

As a clear or pigmented coating for both exterior and interior use.

As water paints that are washable, weatherproof, hard, and durable.

As clear and pigmented primers and sealers for plaster, wall-board, brick, concrete, stucco, paper, fabric, and similar surfaces of the porous type.

For further details, see Chapters 15, 16, and 17, Volume III.

### Types of Drying

The chemical and physical changes which occur in the processing of varnishes or during film formation are many, but the order of sequence in which they occur is so complex in most cases that it has been and still is a debatable question as to what actually transpires. However, it is agreed that some varnishes—spirit varnish—dry mainly by evaporation, whereas the air-drying varnishes dry mainly by oxidation and some polymerization. The baking varnishes dry mainly by polymerization with little oxidation.

**Evaporation.** The conversion of a fluid to a vapor is one change that occurs in the transforming of a liquid varnish into a solid film. Spirit varnishes, cotton solutions, synthetic resin solutions, and the like depend solely upon evaporation of their solvents for film formation. Some solvent type varnishes depend, in part, upon this physical phenomenon.

**Oxidation** is a chemical change which occurs in the preparation of some varnishes and also in the drying of drying oils and varnishes into solid films. Oxidation includes not only the processes in which oxygen is added to a compound but also processes in which hydrogen is withdrawn from a compound. Oxidation, in respect to drying varnishes and drying oils, is generally brought about by the use of oxygen itself taken from the air and usually in the presence of a catalyst.

**Polymerization**, roughly described in the older dictionaries, is the act or process of changing to a polymeric form of higher molecular weight. They give the formation of paraldehyde from aldehyde. In a good many earlier organic chemistry books, a polymerization product is said to be one formed by the union of two or more molecules of the original compound in such a manner that depolymerization or cleavage into the original substance is easily effected. The authors of these books go on to state that this property is peculiar to unsaturated compounds from a natural tendency to saturate themselves. The part of the definition which refers to depolymerization is true only with some polymerized products and was probably the concept held before the advent of synthetic resins and more complex unsatu-

rated compounds. A great many of the polymerized products of today probably cannot be depolymerized without some decomposition because of the affinity of the unsaturated molecules for each other after polymerizing.

In the paint and varnish industry, the idea of polymerization became more active owing to the extensive work in the 1920's on heat-bodied vegetable oils, generally known as polymerized oils. Early writings and bulletins introduced heat-bodied oils in the following manner: The phenomenon of linseed and other vegetable oils to thickening under heat is called polymerization. The art of preparing linseed oil for lithographing inks, enamels and varnish depends on the property of the oil acquiring a high consistency under heat.

Later, in the formation of *synthetic resins* from more complex unsaturated molecules, the theory and controlling factors regulating and promoting polymerization became extensive, complex, and contradictory. However, a survey of various products and theories of polymerization has resolved this reaction to the following tentative generalization so ably set forth in Burk's article on polymerization, *Ind. and Eng. Chem.*, **30**, 1054 (1938).

1. Hydrogen atoms, on the unsaturated link, are necessary for polymerization. An apparent exception is formed by certain halogen-substituted acetylene.
2. Increase in molecular weight eventually reduces polymerization tendencies. The contrary, however, is proposed by Flory and supported in the case of polyester formation in spite of decreased steric factors, decreased velocities, etc., which one would expect as the polymers grow.
3. Substitution of certain groups, such as halogen, vinyl, phenyl, acetylene, carbonyl, and ester groups, vastly stimulates the polymerization of unsaturated hydrocarbons.
4. The effect of substituents depends upon their nature, number, and position, as defined in the following generalizations.
5. Conjugated unsaturation leads to pronounced polymerization tendencies if too many hydrogens are not substituted.
6. Widely separated unsaturated groups approach in their polymerization tendencies those of separate groups. (In some cases, re-arrangement to a conjugated form occurs.)
7. Nonaromatic ring structure containing unsaturation in the ring may have this unsaturation conjugated with side-chain unsaturation. But where the ring is aromatic, carbon-carbon links which involve the ring are not, in general, established during the polymerization.
8. Various unsaturated five-membered ring structures are particularly prone to polymerize.



9. Cyclic olefins with six or more carbon atoms in the ring are comparable with the corresponding open-chain olefins in their tendencies to polymerize.
10. The effectiveness of halogen substitution appears to be in the order iodine > bromine > chlorine.
11. Precise comparison of the polymerization tendencies of hydrocarbons is difficult on account of the catalytic effect of oxygen, and possibly other incidental catalysts, and the effect of light. Varying pressures also add uncertainty to comparisons.

**Condensation.** To condense is defined in various dictionaries as to make more close, compact, dense, or thick; to combine, solidify, boil down, intensify, squeeze, reduce, diminish, etc., all of which apply in some way to chemical condensation. Condensation is the union of two or more molecules or parts of the same molecule (with or without elimination of component elements) in which the new combination is effected between the carbon atoms. It will be observed that the union between molecules or parts of molecules is nearly always determined by unsaturation and by a consequent tendency for the unsaturated atoms to saturate themselves. On this basis, condensation processes may be roughly divided into two groups: those in which the combining molecules are induced to unite by being rendered, as it were, artificially unsaturated as the result of withdrawing certain elements and those which, being already unsaturated, combine either spontaneously or with the help of a reagent or catalyst.

Condensation is the reacting of two or more molecules into one or the formation of a new body by various classes of interaction, attended generally with the separation of water, alcohol, ammonia, or hydrochloric acid, etc.

In the baking and drying of varnishes into films, the process of condensation is involved, and it occurs alone or in combination with oxidation, polymerization, etc.

#### SPIRIT VARNISHES

These varnishes belonged originally to a class which was composed of alcohol-soluble resins of both vegetable and animal origin and alcohol. They dried by the evaporation of the solvent. Sandarac, alcohol-soluble manila, gun elemi, and various forms of shellac were the resins chiefly used in spirit varnishes. Later, other gums and resins were used—rosin, ester gum, and some of the newer synthetic resins. The solvents began to drift from alcohol to alcohol-benzol mixtures or alcohol-petroleum hydrocarbon mixtures. Plasticizers such as

castor oil and tricresyl phosphate improved the elasticity and also enabled harder, cheaper resins to be used in spirit varnishes. The early phenol-formaldehyde resins were not oil-miscible but alcohol-soluble and were thus put on the market as varnishes which were used for both air drying and baking.

Since the advent of synthetic resins, the use of cold-cut solutions has been extensive and has brought to this class of varnishes an inexhaustive supply of raw materials, not only as resins but also as plasticizers and solvents for these resins. The old field of merely air-drying compositions has been extended to low- and high-baking operations, broadening the scope of these cold-cut solutions nearly to that of the varnishes in general.

The term "spirit varnish" should no longer be confined to the alcohol-soluble resins, but should include all cold-cut solutions which contain any number of solvents, plasticizers, stabilizers, and resins. However, for the present, the term spirit varnish still means the solution of a Manila resin in alcohol.

### HOT MELT COATINGS

Wax and wax combinations for coating papers, cloth, etc., have been commonly employed for many years, and their uses have expanded especially for the food package industry where they are satisfactorily used for a number of applications. Food packages could be improved by varnish-like coatings if the cost of the raw materials and the cost of method of application would permit.

Economical coatings, known as hot melt coatings, can be obtained by the use of cellulose ethers, treated rubbers, and moderate-priced synthetic resins. These coatings are applied to paper stocks at high speed. They have exceptionally high coverage or spreading rate for a unit weight.

Hot melt coatings may be produced colored or colorless, odorless and tasteless; of good flexibility with good heat-sealing properties, good adhesion, non-blocking characteristics, and low moisture transmission. All these properties can be modified by varying the proportions of the ingredients; for instance, in employing a hot melt composition such as:

- 10% Ethylcellulose (52% ethoxy content 10 to 15 viscosity)
- 15-20% Phenolic resin
- 30% Paraffin wax
- 30-40% High melting point synthetic wax
- x% Plasticizer (diamyl phthalate or dibutyl phthalate)

Modifications can be made which produce the following characteristics:

Higher temperatures can be used in applying the hot melt coatings when diamyl phthalate is used in place of dibutyl phthalate.

To increase heat-sealing properties, increase ethylcellulose and resin constituents.

To increase resistance to moisture transmission, increase wax.

To increase toughness, increase ethylcellulose.

To reduce tack, decrease rosin and also plasticizer, or increase wax constituent.

To increase flexibility, increase plasticizer.

To decrease fluidity, use higher viscosity ethylcellulose.

To reduce toughness, use lower viscosity ethylcellulose.

These are only a few of the changes that can be made with this simple formulation. Many other modifications are possible owing to the number of other raw materials which can be employed to impart specific properties.

#### VARNISH TESTING

The testing of varnishes is of importance both to the manufacturer and to the user. The testing, by the manufacturer, enables him to establish a reproducible article which will meet desired standards or specifications. The testing of varnishes, by the user, determines the uniformity of products as obtained from the varnish manufacturer.

Standard methods have been developed and adopted for the examination of varnishes by the American Society for Testing Materials. They are A.S.T.M. Standard Method D154-38 for testing oleoresinous varnishes and D115-39T for testing insulating varnishes.

Some of the more important tests are given here. For detailed discussion of each test, see the original specifications, Gardner \* and other original sources. See note at end of chapter.

*Appearance* (A.S.T.M. D154-38). "A thoroughly mixed sample shall be poured into a clear glass bottle or test tube, 1.5 to 2.0 cm. ( $\frac{5}{16}$  to  $\frac{13}{16}$  inch) in diameter to a depth of at least 2.5 cm. The varnish shall then be examined by transmitted light and shall be clear and transparent."

*Color*, 1 (A.S.T.M. D154-38). "A common test method. Reference standard color solutions shall be prepared by dissolving 1, 2, 3, 4, 5, and 6 grams respec-

\* *Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors*, Institute of Paint and Varnish Research, Washington, D. C., 9th Edition, 1939.

tively of pure powdered potassium dichromate in 100 ml. of pure sulfuric acid (sp. gr. 1.84). Gentle heat may be applied, if necessary, to effect the solution of dichromate. Fresh solutions are necessary.

"Since the potassium dichromate-sulfuric acid solutions must be freshly made for this color comparison, it is frequently more convenient to compare samples with a series of permanently sealed tubes of varnish which have been previously found to be lighter in color than the reference standard solutions.

"The reference standard color solutions and a sample of the varnish to be tested shall each be poured into separate thin-walled glass tubes 1.5 to 2.0 cm. ( $\frac{3}{16}$  to  $\frac{13}{16}$  inch) in diameter to a depth of not less than 2.5 cm. The color comparison shall be made by placing the tubes close together and looking through them by transmitted light. If permanently sealed tubes of varnish are used for the color comparison and the sample of the varnish being tested is found to be darker than a standard tube of varnish, final comparison shall be made with freshly prepared potassium dichromate-sulfuric acid solutions.

"The color of the varnish shall be stated in terms of the reference standard (calling the standards No. 1, No. 2, No. 3, etc.) which it is equal to or lighter than in color."

2. Hellige Color Comparator is extensively employed in the varnish industry. Gardner states: "This device employs eighteen colored glass standards mounted in two composition wheels about four inches in diameter. The glass discs were originally selected to match a series of 18 varnishes ranging in color from that of an acid refined linseed oil to that of a solution of 3 grams of potassium bichromate in 100 cc. of sulfuric acid (specific gravity 1.84)." At the time (1930) these standards were selected, it was thought that nine of them would be sufficient. They were numbered 1 to 9. Subsequently, the intervals between the standards were reduced by adding nine more. These were numbered 1L, 2L, . . . 9L. The term "L" indicates that the standard is lighter in color than the corresponding unlettered one. The intervals were determined rather arbitrarily. As a result, the set has not been entirely satisfactory. The tube which has been employed to determine the viscosity, by means of the Gardner-Holdt Bubble Viscometer, is slipped into the middle opening and the wheel is revolved until a color match is obtained. The color number is read at an opening in the box.

*Viscosity* (A.S.T.M. D154-38). "Viscosity shall be determined by comparison at 25° C. (77° F.) with secondary standards whose viscosity expressed in poises has been accurately determined at that temperature. Gardner-Holdt tubes are used generally (*Circular* 178, Scientific Section, Paint Manufacturers' Association of the United States).

*Gloss* (Gardner). "Gloss is the ability of a surface to reflect light regularly. This definition is a general one which covers all the characteristics of regular reflection. However, if one starts to classify and grade the gloss of materials, he will encounter a number of distinctions such as the one noted in the introductory paragraph between objective and subjective gloss. Five of these distinct types of gloss, which are appreciated as gloss but are graded along different scales and by different instrumental applications, are listed below. With each gloss type is a description of the criterion by which it is identified.

"*Objective gloss* is recognized as the intensity of light regularly (specularly) reflected from the surface in question. This type of gloss is independent of the lightness of the surface being measured so that a white and a black of the same

type of paint should have the same objective gloss. This type of gloss is measured by the Hunter Glossmeter and may be measured by the Pfund Glossimeter and others. It is probably the preferred type for exterior house paints, where brush marks interfere with the observation of reflected images and for surfaces of high specular reflection.

*"Subjective gloss* is recognized as the contrast between the specular reflection and the diffuse reflection from the same surface. A black surface reflects almost no light diffusely and so the subjective gloss of black surfaces is always very high. Correspondingly, the subjective gloss of white surfaces is always low. This type of gloss is measured by the Ingersoll Glarimeter, the similar Keiser gloss meter, Jones gloss meter for photographic papers, the Pfund Glossimeter, and many others. Subjective gloss is of greatest interest to the paper industry and is not so important as far as the paint industry is concerned.

*"The sharpness of images* is very widely used in the paint industry, the porcelain enamel industry, and several of the finishes industries as the criterion for gloss. The distinctness and clearness of images reflected in the surface under consideration are the basis on which the surface's gloss is graded. Wolff, Pfund, Ewald, Sward and Levy, Hunter, and the Detroit Paint Production Club have used this criterion as the basis for gloss determinations in the design of gloss meters. It is useful for glossy surfaces, free from brush marks or other interfering texture.

*"Bloom* is a factor which is related to both the sharpness of images and subjective gloss, yet it is distinctly different. Two surfaces may have the same color, the same contrast between the bright areas of specular reflection and the darker areas of diffuse reflection, and the two surfaces may reflect images equally distinctly. From one sample, however, there may be a halo visible about all reflected images, blending from the diffuse into the specular reflection. In contrast, the other surface might reflect clean images. All observers would agree that the surface giving clear, clean-cut image reproduction was glossier than the surface showing a bloom about the lines of image reflection.

No one is known to have measured this factor of gloss, but it is unmistakably present as a characteristic which influences the judgment in evaluating gloss. Bloom may be recorded photographically with a sharpness of image device such as the Hunter Gloss Comparator.

*"Smoothness.* When one has graded many types of surfaces for gloss, he will find if he examines the gradings that the fewer points, particles, scratches, etc., there are on a surface which enable him to detect the presence and exact position of that surface, the glossier the surface will appear. This criterion would be treated as a factor of surface texture except for the fact that so many observers are found to let it influence their judgment of gloss. It would be better to say that this factor describes the smoothness and evenness of surfaces rather than gloss.

"It can be shown that this is the most important factor in accounting for the appearance of 'depth' in finishes. Anyone can try a simple experiment to verify this fact. Consider a clean surface of good 'depth.' Notice how this 'depth' disappears if a few particles of dirt, or scratches, or smears of grease are added to the surface. 'Depth of finish' is appreciated when there are no points on the surface which will enable the eye to easily fixate the surface and allow the observer to recognize where that surface is. The observer's inability to recognize the presence of the surface by the criteria which he usually uses leads him to say that

the grain of the wood or the body of the color appears to be 'down deep below the surface.' In truth he is saying that he cannot see where the surface is, because he can see nothing to recognize it by.

"This gloss criterion of smoothness has apparently not been measured by anyone in the past and it may prove difficult for anyone to measure quantitatively in the future."

*Specific gravity.* The specific gravity is usually determined sufficiently accurately with a Westfall balance, a standardized hydrometer, or a pycnometer. The specific gravity of the varnishes is expressed as the ratio of the weight of a given volume at 25 C. to that of an equal volume of water at the same temperature. For detailed information on methods of determining specific gravity, see the usual physical chemistry book or Gardner's *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors*, 9th Edition, 1939.

*Flash point of volatile flammable liquids (A.S.T.M. D56-36).* The Tag Closed Tester shall be used for all volatile flammable liquids flashing below 175° F. with the exception of products classed as fuel oil. Determination of the flash point of fuel oil by the Tag Tester is permissible, but the Pensky-Martens Tester as described in D93 is to be preferred.

*Setting to touch and drying time* (Specification TT-V-121a, F-2e). (See note at end of chapter.) Flow the varnish on one of the clear glass panels. The panels used in the following tests shall be:

(1) Tin, cut from bright tin plate weighing not more than 25 grams and not less than 19 grams per square decimeter (0.51 to 0.39 pound per square foot). (Commercial No. 31 gage bright tin plate should weigh about 0.44 pound per square foot. It is important that the tin plate used shall be within the limits set.)

(2) Glass, cut from commercial window glass, which shall be clear and free from blemishes.

(3) Glass, cut from what is commercially known as black Carrara glass, one side of which has been polished to a smooth surface. These panels shall be about 7.5 to 13 cm. (3 × 5 inches) and must be thoroughly cleaned with benzol immediately before using.

Place the panel in a nearly vertical position in a well-ventilated room but not in the direct rays of the sun. The atmosphere of this room must be free from products of combustion or laboratory fumes. The temperature of the room should be 21 to 32° C. (70 to 90° F.). The film is tested at points not less than 2.5 cm. (1 inch) from the edges of the film by touching lightly with the finger. The varnish is considered to have set to touch when gentle pressure of the finger shows a tacky condition but none of the varnish adheres to the finger. The varnish is considered to have dried hard when the pressure that can be exerted between the thumb and finger does not move the film or leave a mark which remains noticeable after the spot is lightly polished. If rapid light rubbing breaks the surface, the sample is considered not to have satisfactorily dried hard. In case the test shows time of setting to touch in less than 30 minutes or more than 2 hours or drying hard more than 8 hours, respectively, two additional tests shall be run on different days, and if the varnish does not meet the above drying and hardening requirements on *both* of these additional tests, it shall be considered unsatisfactory. The varnish shall show no tack or pull on the thumb under the pressure that can be exerted on it between the thumb and forefinger at the end

of the 8-hour dry-hard period. In cases where different laboratories fail to agree on the drying test, due to different atmospheric conditions, and umpire tests are necessary, such tests shall be made in a well-ventilated room maintained at a temperature of  $25 \pm 2^\circ \text{C}$ . ( $77 \pm 4^\circ \text{F}$ .) and relative humidity of  $50 \pm 4$  per cent saturation.

*Working properties* (TT-V-121a, F-2g). Coat a smooth clean panel of metal or wood with the sample, using a good varnish brush. Observe whether the varnish shows objectionable "pulling" under the brush and whether the varnish film levels and yields a surface of good appearance.

*Skinning* (TT-V-121a, F-2k). Note condition on opening can. Half fill a clean glass container that is not less than 2 inches in diameter and which can be tightly stoppered (immediately after closing invert for a moment to seal the stopper) with the varnish. Let stand in a dark place for not less than 48 hours, and examine with a spatula. No skin should be visible over the surface. A slight amount of jelly or skin formation where the surface meets the side of the container may be disregarded.

*Odor* (TT-V-121a, F-21). Note odor of liquid varnish, and also during application and after drying.

*Safety of working—Draft test.* (Specification TT-V-121a, F-2h). Flow the varnish on one of the clear glass panels and immediately place the panel in the direct draft of a small (8- or 10-inch) electric fan running at full speed. The panel should be placed approximately 2 feet from the fan in a nearly vertical position and at an angle of  $45^\circ$  to the line of the air current. Allow the panel to remain in this position for 5 hours, remove, and allow to harden overnight. The varnish shall show no dulling, crow's footing, or frosting. This test shall be made under the same room and temperature conditions noted under "Setting to touch and drying time," page 243.

*Gas test. Apparatus.* The necessary apparatus consists of a glass bell jar approximately 20 cm. (8 inches) in diameter and 30 cm. (12 inches) in height, inside dimensions, having a small kerosene glow lamp without chimney or a small alcohol lamp filled with kerosene, using a round wick not over 6 mm. ( $\frac{1}{4}$  inch) in diameter and adjusted to give a flame of 2 cm. ( $\frac{3}{8}$  inch) in height. A metal frame or ring stand is fitted inside the bell jar and provided with a suitable support for holding a disk of tin plate 15 cm. (6 inches) in diameter in a horizontal position, 5 cm. (2 inches) above the wick of lamp. Additional horizontal supports shall be provided for holding the various varnished panels under test. The panels for use in this test are described under "Setting to touch and drying time," page 243.

The form and arrangement of the above apparatus are designed to provide an even distribution of the products of combustion over the test panels.

*Method.* First determine the normal time required for the varnish to set to touch as described under "Setting to touch and drying time," page 243. Divide this time by five to arrive at the different drying periods at which the varnish is to be tested. Thus, if a varnish sets to touch in 1 hour, samples should be tested for resistance to gas at drying periods of 12, 24, 36, and 48 minutes respectively. It is needless to use the fifth or 60-minute period, since a varnish which has set to touch is practically immune to injury from gas fumes. Similarly a varnish which sets to touch in one-half hour should be tested for resistance to gas at drying periods of 6, 12, 18, and 24 minutes, respectively.

*Example.* A varnish which sets to touch in 1 hour is tested as follows: First, clean two of the clear glass panels carefully with benzene. Flow the varnish on one half panel No. 1 at, say, 10 A.M. and allow to drain in a nearly vertical position at room temperature. At 10:12 A.M. flow the varnish on the other half of panel No. 1. Allow to drain as before. At 10:24 A.M., flow varnish on one half of panel No. 2 and at 10:36 A.M. on the other half, as above. At 10:48 A.M. place the two panels in a horizontal position on the upper supports of the frame. Light the lamp and place it on and near the center of the ground glass base plate. Place the bell jar in position in such a manner that it is properly seated. If the chamber is tight and the lamp properly adjusted, the flame will be extinguished in about 4 minutes. After the panels have been in the chamber for one-half hour, remove the bell jar and examine the panels for gas effects.

The varnish on all four sections should remain bright and clear, without trace of pitting, "crow's-footing," frosting, or other defects.

*Percentage non-volatile content.* (A.S.T.M. D154-38). This is an important test, as it determines the amount of solid forming portion of the varnish purchased.

*Test method.* "A portion of the sample of varnish shall be poured into a stoppered bottle or weighing pipette and weighed. About 1.5 grams of the sample shall be transferred to a weighed, flat-bottomed metal dish about 8 cm. in diameter (a friction top can cover is satisfactory). The container shall be weighed again, and the exact amount of weight of the portion of the sample transferred to the weighed dish shall be calculated by difference. The dish with its contents shall be heated for 3 hours in an oven maintained at 105 to 110° C. (221-230° F.). It shall then be weighed after cooling. The ratio of the weight of the residue to that of the sample, expressed as a percentage, shall be taken as the percentage of non-volatile matter in the varnish."

*Water test.* (A.S.T.M. D154-38). "The varnish shall be poured on carefully cleaned tin panels (described under 'Setting to touch and drying time'\*) and allowed to drain in a nearly vertical position and dry for 48 hours. The panel shall then be placed in a beaker containing about 7 cm. (2.5 inches) of distilled water at room temperature, immersing the end of the panel which was uppermost during the drying, and allowed to remain in the water for 18 hours. The panel shall then be removed from the water, wiped carefully, and allowed to dry out at room temperature. The time required for whitening, if any, to disappear, shall be noted.

"Blooming, which sometimes occurs on immersion, is considered as a degree of whitening.

"The results of the water tests shall be reported as follows:

- (a) "Not visibly affected.
- (b) "Whitening disappears within 20 minutes.
- (c) "Whitening does not disappear within 20 minutes, but does disappear within 2 hours.
- (d) "Whitening does not disappear in 2 hours, but does disappear within 24 hours.
- (e) "Whitening does not disappear within 24 hours."

\* The description given here is found in the Federal Standard Specification TT-V-121a, which is the same as that given in A.S.T.M. D154-38, Section 11.



Although the water test is described for cold water, it is often conducted in hot water. In this case, the method is similar to that of cold water, except the time of immersion is shortened to 15 minutes to several hours, depending upon the user's requirements.

The water test is conducted in several other ways than the one given and for specific uses. The test is performed to determine:

1. The appearance and hardness of varnish, before and after immersion in tap or distilled water, over a specific period of time.
2. The decrease in dielectric strength after immersion in water for a definite period of time (see A.S.T.M. D115-39T).
3. The insulation resistance before and after immersion in water maintained at a specific temperature and for a definite period of time.
4. The percentage absorption of moisture for a specific time (Customer specification—private communication).

*Kauri reduction test* (Specification TT-V-121a, F-2j).

*"Toughness.* The toughness of the varnish is determined by the kauri reduction test, as follows: By proportionately reducing its toughness by the addition of a standard solution of 'run kauri' gum in pure spirits of turpentine.

*"Preparation of the 'run kauri.'* Arrange a distillation flask, water-cooled condenser, and a tared receiver on a balance. Place in the flask about one-third of its volumetric capacity of clear, bright, hard pieces of kauri gum broken to pea size. Carefully melt and distill until 25 per cent by weight of the gum taken is collected in the tared receiver. Pour the residue into a clean pan and when cold break up into small pieces.

*"Preparation of standard 'run kauri' solution.* Place a quantity of the small broken pieces of run kauri, together with twice its weight of freshly redistilled spirits of turpentine, using only that portion distilling over between 153 and 170° C. (308° and 338° F.) in a carefully tared beaker. Dissolve by heating to a temperature of about 149° C. (300° F.) and bring back to correct weight when cold by the addition of the amount of redistilled spirits of turpentine necessary to replace the loss by evaporation during the dissolving of the gum.

*"Reduction of the varnish.* Having carefully determined the non-volatile content of the varnish according to the method under 'Percentage non-volatile content' (see page 245) of this specification, take 100 grams of the varnish and add it to an amount of the standard run kauri solution equivalent to 100 per cent, by weight, of the non-volatile matter in the varnish. Mix the varnish and the solution thoroughly.

*"Application of the varnish.* Flow a coat of the varnish thus reduced on one of the tin panels described under 'Setting to touch and drying time,' page 243, and let stand in a nearly vertical position at room temperature for 1 hour. Next place the panel in a horizontal position in a properly ventilated oven and bake for 5 hours at 95 to 100° C. Remove the panel from the oven and allow to cool at room temperature, preferably 25.0° C.

*"Bending the panel.* Place the panel with the varnished side uppermost over a 3-mm. ( $\frac{1}{8}$ -inch) rod, held firmly by suitable supports, at a point equally distant from the top and bottom edges of the panel and bend the panel double rapidly. The varnish must show no cracking whatsoever at the point of bending. For accurate results the bending of the panel should always be done at  $25^\circ \pm 0.1^\circ$  C.

(77° ± 0.2° F.) and a relative humidity of 50 ± 4 per cent saturation, for a lowering of the temperature will lower the percentage of reduction that the varnish will stand without cracking, while an increase in the temperature increases the percentage of reduction that the varnish will stand."

*Acid number* (A.S.T.M. D154-38).

*"Solutions required.* (a) Alcoholic oxalic acid solution (0.1 N). Dissolve 6.3 g. of c.p. oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) in sufficient 95 per cent ethyl alcohol to make a liter.

"(b) Alcoholic potassium hydroxide (0.1 N). Dissolve approximately 6.6 g. of c.p. alcohol refined potassium hydroxide (85.86 per cent KOH) in sufficient 95 per cent ethyl alcohol to make a liter, and standardize in the usual manner.

"(c) Neutral solvent mixture. Mix 75 per cent of ethyl alcohol (95 per cent) and 25 per cent of c.p. benzene (benzol,  $\text{C}_6\text{H}_6$ ).

"(d) Phenolphthalein Indicator. Dissolve 10 g. of phenolphthalein indicator in 1 liter of ethyl alcohol (95 per cent). Use 1 ml. for titration.

*"Procedure.* (a) A 3- to 5-g. sample of the varnish shall be weighed into a 500-ml. glass-stoppered Erlenmeyer flask, 75 ml. of the solvent mixture added and warmed slightly to aid solution. A definite accurately measured quantity (10 to 25 ml.) of the standard 0.1 N oxalic acid solution shall then be added. The mixture shall be refluxed on a hot plate (using a reflux condenser) for about 1 hour, or until the soaps present have been decomposed. The solution shall then be removed and titrated while hot with the standard 0.1 N potassium hydroxide solution using phenolphthalein indicator. As the end point is approached, very vigorous shaking will be required. Titrating while hot increases the speed of titration and results in a sharper end point. A pink coloration which persists for several minutes shall be taken as the end point.

"(b) A blank containing the same quantity of the standard 0.1 N oxalic acid solution should be run using the same procedure as for the sample.

*"Calculation.* The acid number is the weight in milligrams of potassium hydroxide required to neutralize a 1-g. sample of the varnish calculated as follows:

$$\text{Acid number} = \frac{(a - b)c}{w}$$

where  $a$  = milliliters of potassium hydroxide required for the sample.

$b$  = milliliters of potassium hydroxide required for the blank.

$c$  = milligrams of potassium hydroxide per milliliter (value of standard potassium hydroxide solution).

$w$  = weight of the sample in grams."

*Alkali test* (A.S.T.M. D154-38). "A 1- by 6-in. test tube shall be thoroughly cleaned in benzol. The tube shall then be dipped into the sample of varnish and the mouth of the tube inverted downward immediately and the varnish allowed to dry for 48 hours in an atmosphere free from dust, drafts, products of combustion, or laboratory fumes. The temperature of the room during the drying period shall be 65 to 78° F. (19 to 25° C.). The varnish-coated tube shall then be suspended in a solution of sodium hydroxide (3 per cent) maintained at 70 ± 2 F. (21 ± 1.1 C.). The tube shall then be removed after desired periods of time, such as 8, 16, 24, and 48 hours, and the varnish examined for whitening, blistering, or removal. Before making the examination, the varnished tube shall

be rinsed under a gentle stream of water and allowed to air dry for 30 minutes."

*Resistance to reagents.* Same as for the alkali test or see Gardner.

*Reagent test.* Four-ounce glass jars having a two-inch lug cap are used for this test. The varnish to be tested is applied to a flexible base, preferably a supercalandered Kraft paper, and baked at the specified temperature for the specified time suitable for the test varnish. The coated specimen is cut to fit the jar cap and inserted in the cap over a suitable backing to give a tight seal when the cap is placed on the jar. Fifty centimeters of the test reagent are placed in the glass jar and the jar is capped so the coating on the test specimen will be in contact with the reagent. The sealed jars are set in a horizontal position so that half of the coating is in contact with the liquid and the other half is in contact with the vapor. After a test period of seven days at 105° F. (40.6° C.), the jars are removed from the oven, cooled and the specimens examined.

*Imprint test* (Gardner, page 119). "Coatings for chairs, desks and other furniture often appear hard, but when subjected to continuous pressure yield enough to be seriously marred. This may take place during shipment or subsequent use. A simple method of testing the imprint resistance of coatings is by means of a weight, which gives a load of 2 pounds per square inch. In order to distribute the weight over uneven surfaces, a piece of felt is cemented to the under side of the weight. A piece of smooth cheesecloth is placed between the weight and the surface under test. Print resistance may be evaluated by the load required to make an impression within a given time, or the time required with a given load, or by comparing the imprint under identical loads and duration of test."

For the testing of insulating varnishes for electrical insulation, see A.S.T.M. D115-39T (1939).

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The editor wishes to acknowledge gratefully the helpful criticism and suggestions, and assistance given by Messrs. Henry J. Stalzer, Frank J. Hahn, Merwin J. Eberley, and Dominick D. Razzano of his own staff.

*Note:* The time requirements referred to under Test Methods, "Set to Touch and Drying Times," "Water Test," etc., are only relative values and would vary for other specifications and other types of varnishes. These test methods have been chosen mainly to be used as a guide for test procedure for preparing panels, and for noting the end point of each test.

## CHAPTER 9

### WRINKLE FINISHES

HOWARD R. MOORE

#### General Considerations

Wrinkle finishes are "textured enamels," as contrasted to orthodox, plain finishes. They form an uneven surface of regular pattern upon baking. They are also known as crinkle, shrivel, ripple, and suède finishes. The twelve cuts illustrate several different patterns of wrinkle finishes. They belong very definitely to the class of novelty finishes which includes crystal, crystallizing enamels, crystallizing lacquers, and hammer finishes. However, the greater emphasis that is now being placed on wrinkle finishes may be due to the fact that they actually have protective as well as ornamental functions. Crystal finishes are deficient in protective action because they consist of areas with a number of polygonal lines which may be broken off, thus permitting moisture to penetrate to the underlying metal. In spite of their surface irregularity, wrinkle finishes, on the other hand, have a continuous film which is resistant to impact and protects the metal substratum from rust.\* Faucett (6) has given an excellent summary of the main characteristics of various novelty finishes, and no attempt will be made in this review to discuss them, except to show the relationship of the crystallizing type of enamels to wrinkle finishes.

The production of wrinkle finishes exceeds greatly that of all other novelty finishes. This may be due to the fact that their textured character adapts them to flexible supports such as fabrics, cloth, and paper, as well as metal and wood. Reliable reports indicate that the present total gross annual production is in the range of two to three million dollars per year. As announced in 1938 (17), existing patents owned by three industrial companies † were pooled and purchased by

\*In reviewing the manuscript, New Wrinkle, Inc., has brought forth this interesting comparison between the protective coating efficiency of wrinkle and crystal finishes.—Editor.

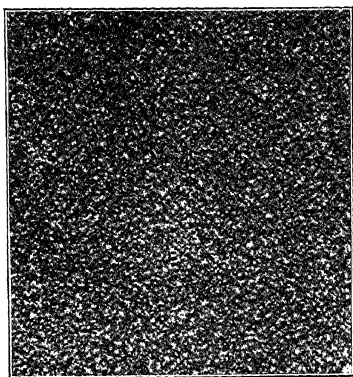
† Chadeloid Chemical Company, New York, N. Y.; Kay and Ess Chemical Corporation, Dayton, Ohio; Kay and Ess Company, Dayton, Ohio.

one company.\* Because of the publicity sponsored by this company, wrinkle finishes have been recognized as useful protective and decorative coatings.

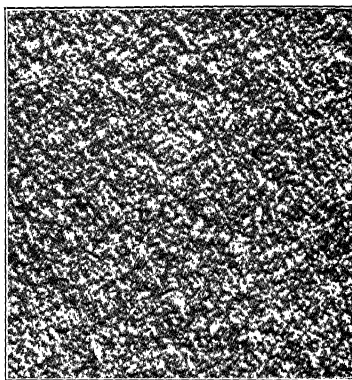
The early investigators concentrated their efforts on methods to control the wrinkling properties of tung oil and undercooked tung oil varnishes. The tendency to erratic, non-reproducible patterns was apparently due to the inherent frosting characteristics of tung oil which many workers sought to eliminate. Prior to Dr. F. B. Root's pioneering work on oil resin ratios and blown oils, very little progress was made in controlling wrinkling tendencies. In a certain sense, therefore, the early workers actually capitalized on the wrinkling defects of tung oil and improperly made tung oil vehicles. Because these early formulas required greater than normal thickness to insure wrinkling, they have not enjoyed the scientific status of modern smooth-surface organic finishes. Recent advances in the art of manufacture, however, have succeeded in overcoming the handicap of abnormally high thicknesses to guarantee wrinkling, so that the older interpretations of the wrinkling phenomena have had to undergo revision. The necessity of more adequate theories has also been emphasized by the production of new compositions free from tung oil and other conjugated oils. Furthermore, recent developments in texture have definitely improved the "eye appeal" of the finish.

Comparative tests with older types of oleoresinous wrinkle finishes have shown that these new compositions are definitely superior in the matter of marproofness (abrasion resistance), soilproofness (grease, dirt, and perspiration resistance), and adaptability to irregular surfaces without the need of priming coats. The interpretation of the wrinkling mechanism of these improved low thickness wrinkle compositions constitutes a definite challenge to current views on the thermal and chemical conversion of organic polymers. Indeed, it may be supposed that a unitary theory of the curing of enamel films should also include the wrinkling phenomenon as a limiting case. In other words, it appears that a close study of the relation of wrinkling to enamel composition factors, on the one hand, and application conditions, on the other, will contribute to a better understanding of the factors affecting the curing of orthodox enamel finishes. Taking into consideration these close relations of wrinkling to the usual conversion processes of oxidation and polymerization of ordinary films, it is clear that a better understanding of the wrinkling phenomenon is mandatory for investigators of protective coatings.

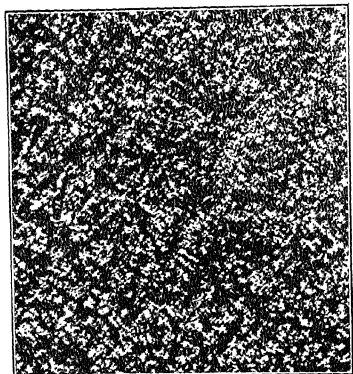
\*New Wrinkle, Inc., Mutual Home Building, Dayton, Ohio.



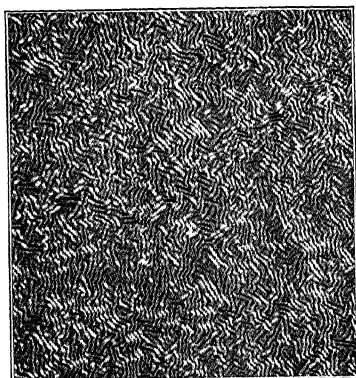
Uniform Wrinkle, Very Small



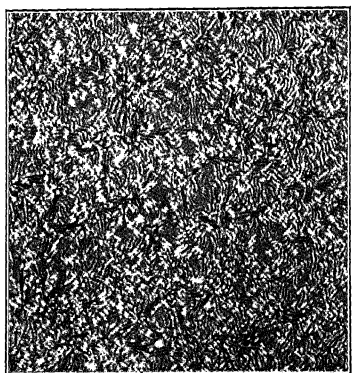
Uniform Wrinkle, Small



Uniform Wrinkle, Medium



Uniform Wrinkle, Heavy



Uniform Wrinkle, Extra Heavy

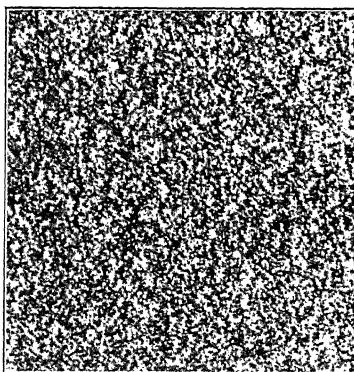


Sag Wrinkle, Medium

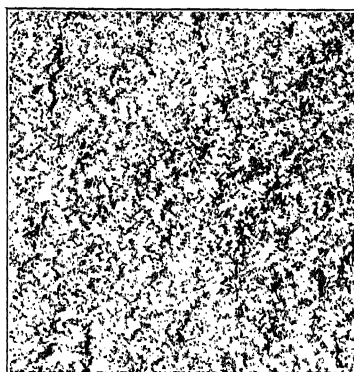
*Courtesy of New Wrinkle, Inc.*



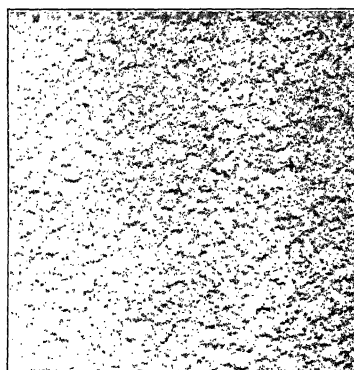
Pine Tree Wrinkle, Medium



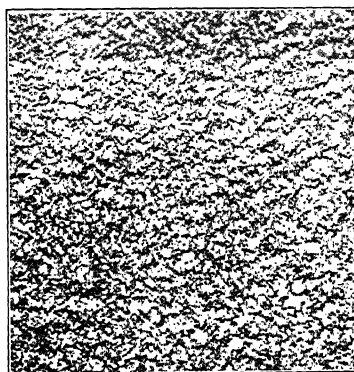
Opalescence Wrinkle, Fine



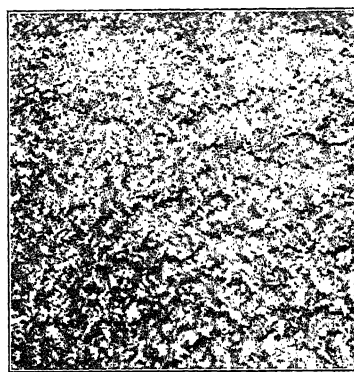
Opalescence Wrinkle, Medium



Birdseye Wrinkle, Fine



Birdseye Wrinkle, Medium



Birdseye Wrinkle, Heavy

*Courtesy of New Wrinkle, Inc.*



A cursory review of the wrinkle finish patent literature has shown that a chronological review of these patents, with detailed comments on the compositions and procedures used, would be valueless. Indeed, a historical survey as measured by the dates of issuance of the various patents would be misleading and probably fail to reveal significant trends in this development. An attempt will be made, however, to classify these various patent disclosures from the viewpoint of the relative emphasis they place on vehicle compositions and practical criteria of good wrinkle finishes. In reviewing the twenty-five odd United States and Canadian patents on this subject, the casual reader must be struck with the frequent emphasis on new types of wrinkling compositions claimed, with little or no emphasis on the relation of these new compositions to processing technique, application conditions, appearance, and physical properties of the resulting finish. In the great majority of cases, a manufacturer dependent on instructions from the patent literature alone would be helpless in developing a set of formulas of prescribed characteristics. This situation is not due to deliberate machinations of secrecy by the various inventors but rather to the inherent complexity of the wrinkling phenomenon and its dependence on a great number of factors. Before attempting to present a critical survey of the patent literature, an attempt will be made to discuss the current ideas of wrinkling formation and the various factors controlling wrinkle finish texture.

### **Mechanism of Wrinkling—Current Theories**

The primary explanation proposed by Morrell (16) for the wrinkling of tung oil films, namely that these films wrinkle on account of the rapid expansion of the outer layer, has been adopted by Bradley (2) and Root (31) as a basic mechanism governing the wrinkling of alkyd enamels. Thus, Bradley states that the underlying portion of the film is fairly fluid whereas the surface is rapidly oxidized to the solid stage. This inequality of hardness sets up strains within the film, resulting in wrinkling. According to Root, a surface oxide forms a surface skin. This surface skin expands laterally, owing to the increase in volume caused by oxidation. The surface then folds into continuous ridges and creases, running over the entire surface. This view assumes that the rate of oxidation conversion of the outer film layer greatly exceeds the rate of polymerization conversion and that the transfer of oxygen from the surface layer to the inner part of the film is both slow and incomplete. The theory originally propounded by Morrell intimates that the third reaction in this series, resulting in

thorough film hardening, is delayed by a second intermediate reaction. Thus, with *A* representing the wrinkle finish vehicle, the following sequence of reactions is supposed to take place:

- (1)  $A + O_2 \rightarrow AO_2$  (This corresponds to surface film oxidation.)
- (2)  $AO_2 + A \rightarrow 2AO$  (This corresponds to the suboxide formed in the interior of the film.)
- (3)  $2AO + O_2 \rightarrow 2AO_2$  (This corresponds to the diffusion of oxygen throughout the film and also reaction of oxygen with the intermediate compounds to give the completely oxidized vehicle.)

Although the foregoing explanation might appear valid for abnormally thick films, it clearly loses its validity for films of normal thickness. The thinner the film, the more is the rate of diffusion of oxygen independent of film thickness. Recent developments (15) indicate that wrinkle finishes can be formulated which show distinct evidence of wrinkling for films of normal enamel thickness.

The following data, procured by the author in 1936, indicate that wrinkle enamel films approaching normal enamel thickness can be obtained. These data were procured with enamels of 50 per cent. non-volatile, using a Pfund depth gage (7) to measure the wet film thickness. Although the accuracy of these results may be seriously called in question, all readings were made at the same time, after spray application with formulas containing the same thinners. More reliable results, of course, would have been obtained if the dry film thicknesses had been measured after baking with the new General Electric film thickness gage.

#### WET FILM THICKNESSES

- |  |           |
|--|-----------|
| 1. Gloss black plain alkyd enamel . . . . .  | 0.012 mm. |
| 2. Gloss black wrinkle enamel, made from<br>aerated resin, Moore (15) . . . . .            | 0.015 mm. |
| 3. Gloss black wrinkle enamel, made from<br>alkyd resin, Bradley (2) . . . . .             | 0.036 mm. |
| 4. Gloss black wrinkle enamel, made from<br>oleoresinous vehicle, Phillippi (19) . . . . . | 0.072 mm. |

In order to obtain the foregoing data, a number of panels were sprayed of variable thicknesses, and the wet film thicknesses noted for those specimens for which wrinkling just occurred. In other words, these data represent the film thickness thresholds at which "slick spots," "shiners," or "fish eyes" just appear. In interpreting

these results, it seems that Morrell's film thickness mechanism would apply most closely to No. 4 oleoresinous enamel. The thickness factors (minimum thicknesses to guarantee wrinkling), however, show decreasing importance for enamels No. 3 and No. 2. The fast-cooking schedules reported by Bradley (2) indicate that underpolymerization is a factor, whereas the cooking schedules reported for reference (15) suggest that the large molecular size of secondary resin polymers is also responsible. Moore states (15) that theories emphasizing abnormal film thickness as a cause of wrinkling should be supplanted by some sort of "strain theory," by which it is conceived that mechanical strains in the film due to lateral and transverse forces occasioned by baking unsymmetrical polymers are a governing factor. The frosting effects of tung oil could not contribute to wrinkling under these circumstances, since tung oil monoglycerides are formed during the cooking process. Ulrich (37) reports that the cooking of tung oil with glycerol completely gasproofs the oil.

The fact that tung oil is required for the older types of wrinkle finish compositions suggests that the wrinkling observed is a cross between tung oil frosting and genuine wrinkling due to high film thickness. Hyman and Greenfield (10) state that the wrinkling of tung oil is due to minute quantities, four to five parts per million, of nitrogen dioxide in the atmosphere. Oven gases, of course, would sensitize all compositions containing raw tung oil or incompletely gasproofed tung oil. Crystal finish compositions (5, 6, 8, 9, 32) depend on an appreciable quantity of raw tung oil in the composition, and it is necessary to subject such finishes in a fouling oven to a temperature of 140–158° F. (60–70° C.) before baking at 230–300° F. (110–149° C.) to harden the film. This frosting phenomenon, however, cannot contribute to the wrinkling of many improved oleoresinous and alkyd wrinkle enamels that wrinkle in an electric oven where fouling gases are absent.

Thus, while the presence of raw or undercooked tung oil must certainly be considered a factor in the wrinkling phenomenon, it seems clear from the above discussion that the factors cited above (low polymerization, size of polymer) must also be taken into account. With regard to size of polymer, Root (22, 30; 31) and Moore (15) have shown that the aeration or blowing of oleoresinous and alkyd polymers intensifies wrinkling. This may be due to the fact that larger polymers are formed by the fixation of oxygen. These oxidized polymers may then associate to give polymers of still higher molecular weight which show improved wrinkling tendencies because of their large size.

No data are available, however, to check this hypothesis since colloidal research has not yet undertaken measurements of the micelle size of varnish or alkyd polymers.

### **Basic Properties of Satisfactory Wrinkle Finishes; Factors Controlling Textures**

The foregoing mechanisms of wrinkling are only theories, valuable insofar as they point the way to new products and processes to improve the desired attributes of satisfactory finishes. Control in texture obviously should be included as one of the basic factors by which the excellence of a wrinkle finish should be evaluated. The present status of the art has advanced to the point of making possible a reasonable control of texture, and this presupposes a reasonable understanding of many other factors controlling formation of the finish. The following list of characteristics is based on application technique as well as inherent characteristics of the enamel composition:

1. Satisfactory hardness.
2. Minimum dirt collection (no flashing, shiners, fish eyes, or slick spots); smooth ornamental appearance.
3. Uniformity of film texture in all colors (relatively insensitive to different kinds of pigments; the same wrinkling effect should be obtained at a given pigment volume ratio for all colors).
4. High covering power or mileage (this means that wrinkling should be positive in small facets and crevices).
5. Fast-baking schedules at the relatively low temperatures of 200–250° F. (93–121° C.).
6. Adaptability to small variations in production technique (gives same wrinkle pattern in various parts of the oven and tolerates a variable air-drying period before entering the oven).
7. Independence of wrinkle pattern on reasonable variations in film thickness (this gives latitude in the thickness applied by spray application).
8. Easy workability (low spray body viscosity facilitates easy atomization with the spray gun).
9. Texture control.

Estimates of the relative importance of the above factors would be very helpful in making comparisons between different vehicles and in formulating the minimum requirements of a satisfactory vehicle.

It has been found in comparing a wide variety of vehicles that the above characteristics prevail only if the wrinkle finish compositions meet the following general requirements:

1. They should not be overpolymerized.
2. Wrinkling should occur with a minimum concentration of top driers, cobalt, and manganese.
3. Wrinkling should occur with a relatively high proportion of low evaporating solvent.
4. Wrinkling should occur in electric as well as in gas-fired ovens.

A brief consideration of the above factors shows that texture control is dependent on composition, processing, and application factors. Pigments, resins, oils, solvents, and driers (kinds and amounts) are composition factors; time, temperature of heating, and aeration are processing factors. Film thickness and baking temperature are application factors. Film thickness, of course, is controlled by the operator, although viscosity and sprayability determine the type of spray job obtained. The temperature of baking is also controlled by the operator. The higher the temperature, the smaller the wrinkle pattern, although it is desirable to choose those compositions that show the least sensitivity to high temperatures.

The increasing control of texture made possible with the newer compositions has enabled some firms to standardize on their wrinkle finish patterns. There is an increasing tendency to issue both large and small texture patterns in all colors. Intermediate wrinkle patterns are usually discouraged, since they complicate the vehicle inventory and add to the formulator's difficulties. However, it is clear that the ability to establish conditions to give fairly uniform patterns in all colors is an achievement of merit and indicates a fundamental understanding of this complex finish.

Recently (since 1939) there has appeared to be a greater tendency to favor the small wrinkle patterns or "suède" finishes. This texture is more pleasing than the deep corrugation of the early oleoresinous patterns. These newer compositions achieve differences in texture by controlling the composition and processing factors mentioned above, rather than the application factor of film thickness alone. Although many patents emphasize the control of texture by varying the vehicle, considerable progress has been made in producing wrinkle finishes of variable pattern by the use of extenders and preferred pigment combinations. Thus, Toll (34) states that a uniform crinkled design may be obtained in various colors by incorporating a "stabilizing agent."

Lithopone, titanium dioxide, and zinc oxide are listed as stabilizers which produce substantially uniform patterns in wrinkle finishes of all colors. In the matter of producing uniform texture with extender pigments, interesting results have been recently obtained (20) by using "Multifex," a colloidal calcium carbonate having an average particle size less than one-tenth of a micron. It is claimed that low sheen finishes of the suède type are readily produced by increasing the ratio of Multifex extender to hiding pigment.\*

### Critique of Wrinkle Finish Patents

Sward (33) has given a brief but adequate review of patent references (1, 2, 4, 8, 9, 18, 19, 21-31, 34-36). As pointed out by Sward, the decorative possibilities of wrinkle and crystal finishes were recognized as early as 1921 (33) by the Moller and Schumann Company of Brooklyn, New York, now known as the Hilo Varnish Corporation. "Crystallization lacquers," evidently baked crystal finishes, were put on the market under the trade name Windowfrost at that time. Dr. F. B. Root was the first, however, to patent his findings on wrinkle finishes. Through the efforts of Root and his coworkers, fifteen patents have been issued. Root is the author of eleven of these patents, Toll, three, and Agnew, one. Other investigators have made the second largest contribution of patents, including four by Kittredge and collaborators, two by Phillippi, and one by Moore. All these patents, with the exception of Bragdon's U. S. Patent 2,048,632 (3) and Burgman's U. S. Patent 1,934,034 (4), have been purchased by New Wrinkle, Inc., U. S. A., which now grants the licenses for the making of finish vehicles and enamels.

The entire list of patents may be roughly classified according to whether their compositions are intended for metal or wood or for flexible supports, such as leather, paper, and fabrics. These compositions are more explicitly intended for fabrics and paper—(1, 11, 13, 14, 31, 35, 36).

Although a detailed study of wrinkle finish patents in their chronological order will not reveal a very systematic development, Sward (33) does seem justified in diagnosing the general trend as a gradual improvement in controlling the baking speed and the character of the wrinkles. In general, the majority of these patents are deficient in giving adequate information on the cooking schedules adopted to make the various vehicles. Information on time and temperature of

\*Private communication, C. W. Blacketer, Diamond Alkali Company.

heating is very scanty; but such details are very important, since overpolymerization will eradicate wrinkling tendencies. These patents (2, 15, 18, 19) are much more explicit in this respect than the average. It is regretted that the authors of the earlier patents did not give more definite information on cooking cycles, since these details would permit a clear differentiation between wrinkle vehicles and orthodox vehicles. With this lack of information, however, it may not be too wrong to state that the various compositions wrinkle because of excess drier and great thickness; not because of any special intrinsic wrinkling tendency. Bradley (2), however, has given cooking schedules which lead one to suppose that his alkyd vehicles are decidedly underpolymerized. Moore (15) states that overpolymerization eliminates wrinkling. The title of Moore's patent (15), "Methods of Producing a Resin," is somewhat misleading and would not ordinarily, therefore, insure its classification with a wrinkle finish patent survey. However, this patent takes cognizance of the great majority of the desirable properties of wrinkle finishes mentioned above and attempts to correlate these desirable properties with the composition and method of manufacture. Earlier patents accomplish the same objective to a lesser degree, but in correlating composition with other desired characteristics they tend to emphasize control of texture to the exclusion of other valuable properties.

The early oleoresinous patents show the following general characteristics:

1. High drier concentration (0.2 to 1.2 per cent manganese or cobalt metal and 2 to 4 per cent lead metal on the resin or varnish solids).

2. The use of specific "wrinkling resins" and "specific wrinkling oils," as contrasted to non-wrinkling ingredients. With regard to wrinkling inhibitors, patent (21) mentions rosin, nitrocellulose, and gilsonite. Rosin cancels wrinkling because it reacts with tung oil according to the diene reaction. A good wrinkling resin will insure a satisfactory finish with only one part of oil to two parts of resin. This corresponds to a six-gallon varnish. It should be noted, however, that a wrinkling alkyd resin may be obtained with only 15.7 per cent linseed fatty acids as the oil-modifying constituent (31). This corresponds to only a three-gallon varnish, assuming that glycerol phthalate is the resin constituent. This classification of wrinkling resins is manifestly arbitrary, since it makes no attempt to classify them from the viewpoint of a fundamental property, such

as their action in gasproofing wood oil or other conjugated oils. Other things being equal, it is believed that synthetic or natural resins that do not have any accelerating effects on the rate of bodying of wood oil are preferable. On theoretical grounds, it is to be expected that resins that retard the bodying of wood oil are most suitable for oleoresinous compositions. Such resin oil-dispersions would probably insure the best cooperation of the inherent frosting action of the tung oil with other wrinkling properties of the finish.

3. With respect to wrinkling oils, it has been stated (30) that both blown and unblown tung, linseed, and perilla oils are preferable. The non-drying or semi-drying oils inhibit wrinkling. Varnish wrinkle compositions may be produced with oil lengths of six to thirty-five gallons. The long-oil varnishes are obviously more suitable for flexible supports, although it has been found desirable (13) to add organic plasticizers for paper "imitation leather" coatings.

Patents numbers (2, 15, 31) summarize the published information on alkyd wrinkling compositions. The pure oil modified types have been covered by Bradley (2) and Root (31), and Moore (15) has covered the more complex secondary alkyd polymers. Root soon recognized the deficiency of the pure oil modified types with regard to hardness and attempted to correct their deficiencies by adding cold cuts of various natural and synthetic resins (congo, ester gum, modified phenolics \*). This method, however, is not satisfactory, since it tends to level out the finish. The novel feature of patent (15) is that the primary resin may be incorporated with the other constituents of the alkyd in such a way as actually to enhance wrinkling ability. In order to assure good package stability, it is recommended that the pigments be ground in a short-time polymerized vehicle, and the pigment paste then thinned down with an aerated vehicle having the same constitution as the grinding vehicle.

Aeration has also been employed by Root (31) to a pure oil modified alkyd. Iodine numbers of secondary alkyd resins (15) are reduced by blowing, indicating the formation of peroxides at the double bonds. The higher viscosity may be accounted for by the association of these resin peroxide bodies by virtue of their polar character. Some such

\* Modified phenolics consist of ester gum modified with phenol formaldehyde condensation products, or a mixture of phenol formaldehyde condensates dispersed in rosin subsequently esterified with glycerol.



mechanism must prevail, since it has been found that thermal polymerization is practically negligible at 350° F. (177° C.), the temperature of aeration. Wrinkling intensity shows a rapid increase with viscosity of the aerated resin, indicating that large polymers are actually advantageous under these circumstances. Hence, it would seem that aerated polymers show increased wrinkling power because of their size and complicated structure, although it is possible that oxygen may be evolved at the temperatures of baking and thus enhance the wrinkling effect.

Details on five typical examples of wrinkle vehicle compositions with cooking schedules are given as follows:

**1. Oleoresinous (Short Oil):**

Pale bold congo .....	100 lb.	
Tung oil .....		15 gal.
Manganese resinate .....	2.0 lb.	
Toluol .....		22 gal.

**Procedure.** Run congo to 625° F. (330° C.), drop to 600° F. (315° C.), regain 650° F. (343° C.); three heats until melted. Add wood oil, gain 550° F. (288° C.), hold 2 minutes. Add precipitated manganese resinate. Cool rapidly with water and reduce.

**2. Oleoresinous (Long Oil).** This composition is adapted to both rigid and flexible supports. It is essentially similar to Phillippi's formula given in patent reference (19).

Modified phenolic resin .....	100 lb.	
Tung oil .....		29.4 gal.
Linseed oil .....		3.35 gal.
Litharge .....	5.2 lb.	
Manganese linoleate .....	12.6 lb.	
Cobalt linoleate .....	3.0 lb.	
High-flash naphtha .....		13.3 gal.
Light petroleum naphtha .....		13.3 gal.

**Procedure.** Heat oils to 470° F. (243° C.), add litharge, hold at 560–570° F. (293–299° C.) for 30 minutes. Stir in linoleate driers and then add modified phenolic resin. Hold at 500° F. (260° C.) until the gum is completely dispersed. Total cooking time, one hour; per cent solids, 67.5.

**3. Alkyd (Pure Oil Modified, Medium Oil Length [2]).**

Glycerol .....	75 lb.
Phthalic anhydride .....	48 lb.
Linseed fatty acids .....	85 lb.
Tung oil .....	85 lb.

Cobalt naphthenate (6% metal) .....	3.3 lb.	
High-flash naphtha .....		18.20 gal.
Toluol .....		18.20 gal.

**Procedure.** The four components of the alkyd are heated to 465° F. (240° C.) for 45 minutes in a non-oxidizing atmosphere. The batch is then cooled to 300° F. (149° C.) and thinned with coal tar thinners. Sufficient drier is added to correspond to 0.05 per cent cobalt on the resin solids. This composition should be thinned to about 40 per cent solids for direct spray application.

**4. Secondary Alkyd (Unitary Resin Made in One Operation [15]).** The following composition is used for both the pigment grinding vehicle and the wrinkle vehicle subsequently added to the paste:

Modified phenolic resin .....	14.4 lb.	
Tung oil .....	41.2 lb.	
Linseed fatty acids .....	10.4 lb.	
Glycerol .....	12.6 lb.	
Phthalic anhydride .....	21.4 lb.	
Varnish makers' and painters' naphtha .....		7.6 gal.
Toluol .....		7.0 gal.

**Procedure for the Grinding Vehicle.** Charge the kettle with the first four constituents and raise the temperature to 490° F. (254° C.) in 20 to 25 minutes in the presence of an inert gas stream. Hold at 490° F. (254° C.) 20 minutes for complete dispersion of the modified phenolic resin. Cut off the fire, let cool to 460° F. (238° C.), and add the phthalic anhydride over a 10-minute period. Increase the heat to prevent the temperature from dropping below 420° F. (215° C.). Raise to 437° F. (225° C.) and hold 45 minutes until the acid number of the secondary resin is 20 or less. After cooling the batch to 325° F. (163° C.), thin to 50 per cent solids.

**Procedure for the Wrinkle Vehicle.** Prepare a duplicate batch, but instead of cooling to 325° F. (163° C.) and thinning, aerate the batch for 2 to 4 hours until the viscosity of a 60 per cent test sample in toluol is N to P (Gardner-Holdt). Do not permit the temperature to drop below 325° F. (163° C.) during the aeration procedure. As soon as the proper viscosity is reached, discontinue the aeration and thin the batch to 60 per cent solids with the same combination thinner.

**5. Secondary Alkyd (Varnish-Alkyd Resin Dispersion Made in One Operation).** The composition is similar to No. 4 above, except that a finished alkyd is added to the resin-oil dispersion. This vehicle does not insure so rapid a wrinkle enamel baking schedule as No. 4 above.

Modified phenolic resin .....	100 lb.
Tung oil .....	78.3 lb.
60% oil modified alkyd (linseed or fish) .....	68 lb.
Low-boiling petroleum naphtha .....	20 gal.
Toluol .....	17 gal.

**Procedure for the Grinding and Wrinkle Vehicles.** Heat the modified phenolic resin and tung oil to 500° F. (260° C.) in one-half hour; hold 10 minutes at 500° F. (260° C.) and check with preheated solid alkyd (no thinner). Hold at 440° F. (227° C.) for 10 minutes until the alkyd is completely dispersed in the varnish. Cool to 325° F. (163° C.) and thin. The wrinkle vehicle is prepared in the same manner, but, instead of cooling to 325° F. (163° C.) and thinning, the resin solution is aerated on the down heat. This permits a 40-minute period of aeration before the temperature is reduced to 325° F. (163° C.). The composition is then thinned to 60 per cent solids with a 50 : 50 mixture of low-boiling petroleum naphtha and toluol.

### Recent Developments and Research Trends

The trend of recent developments is toward faster production schedules with greater hardness. Shorter baking times, of course, produce notable economies. The use of infrared radiation as an auxiliary to conveyor ovens has been claimed to reduce the baking time from 1 hour to 15 or 20 minutes. The finished articles may then be handled for assembly and packing one-half hour later. This technique has been emphasized (20). Short infrared radiation is claimed to produce more rapid solvent elimination. This may be because local heat is concentrated on the wrinkle enamel film itself, and it is, therefore, not necessary to heat up the film support to oven temperatures before securing wrinkling. Although steel has excellent thermal conductivity, the usual process dependent on thermal equilibrium of metal objects with the average oven temperature requires considerably more time, even with forced air circulation. In speeding up baking times, it may be possible also to replace the modified phenolic type of resin by the new urea and melamine resins which promote better flexibility, film hardness, and toughness. While urea-formaldehyde resins actually inhibit wrinkling under most circumstances, some method of compounding may be worked out to utilize their excellent heat-hardening properties.

There is also a notable attempt to procure a better control of texture by improvements in application technique. This may be achieved

by a closer regulation of both atomizing air and fluid pressures as pointed out by the manufacturers of spray equipment (20). In the matter of producing wrinkling compositions of more positive wrinkling behavior, it is imperative to develop a reliable means of measuring the film thickness thresholds for which wrinkling just occurs. It is believed that this may be accomplished satisfactorily with the new General Electric film thickness gage. The development of a reliable technique for measuring wrinkle-film-thickness-thresholds is clearly necessary to measure the degree of improvement claimed by new products and processes.

In providing new baking compositions of better wrinkling tendencies, it may be worth while to study aeration problems more thoroughly. More pronounced effects might be obtained by aerating with oxygen alone, oxygen-ozone mixtures, and oxygen mixed with nitrogen dioxide. It is highly probable that nitrogen dioxide will intensify wrinkling, since Hyman and Greenfield (10) have shown that minute traces of this gas are responsible for the wrinkling of raw tung oil. In this connection, it has been found that a wrinkle of very fine texture can be produced by adding an alcohol solution of sodium nitrite to secondary alkyd wrinkle enamels. This very fine texture is procured only on baking at temperatures of 300° F. (149° C.) and above, and it is believed that sufficient nitrogen dioxide is released by thermal decomposition of sodium nitrite at this temperature to augment wrinkling.

The development of satisfactory air-dry wrinkling compositions will do much to increase the scope of this novelty finish and make it applicable to larger objects that cannot conveniently be baked in a conveyor oven. Here again, a profitable approach may be the development of compositions that show a pronounced wrinkling tendency for small thicknesses. It has been demonstrated that the beta isomer of tung oil (beta elaeostearin) is mainly responsible for wrinkling and that acetone extracts of tung oil remove this ingredient. Hence it would seem that the manufacture of special air-dry compositions from this beta isomer might be worth while. Likewise, the preparation of special extracts from other conjugated oils, such as dehydrated castor and oiticica oils, may yield wrinkling compositions of high potency. A study of wrinkling effects in an inert gas atmosphere should demonstrate the importance of oxygen conversion for the newer types of aerated compositions. Such new evidence might encourage trials with several recognized oxidation and autoxidation catalysts outside the province of conventional metal driers.

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## OLEORESINOUS PAINTS



## CHAPTER 10A

### EXTERIOR FINISHES

WESLEY G. VANNOY

#### House Paints—History

Evidence is found of the use of decorative and protective coatings in very early times. For example, it is recorded that pitch was used by Noah to cover both the inside and the outside of the ark. Jeremiah made reference to a house ceiled with cedar and painted with vermilion, and paint compounds are known to have been used to decorate the tombs of the Egyptians as early as 2500 B.C. (56).

According to Tiemann (66) imitation of the colors found in nature was one of the earliest arts of man. Pigments of one sort or another were known to the rudest nations of antiquity, and every civilization had its colors and its painters. The gaudy colors of the Egyptian and the Hebrew were succeeded by the brilliant tints and lead-bodied oil paints of the Roman and the Greek.

Between the early civilizations which developed the painter's art and the later era which resumed and carried it to still greater prominence, however, is the long break of the dark ages, when Europe relapsed into the barbarism of feudal strife. The fourteenth and fifteenth centuries saw the return of many of the peaceful arts and among them that of the painter.

Apart from its artistic application, the use of paints increased slowly in Europe. Gradually houses and ships took color under the painter's brush, woodwork was preserved by its use, and ornamentation by colors became general. The manufacture and the application of paint had become established and recognized industries, and they were of considerable importance at the time when the great English companies began dispatching colonists to the shores of the New World.

Paint and painting practices were decidedly unpopular in the early colonial days. Tiemann records that the early American settlers had small use for paint in the wilderness they came to conquer. Log cabins and the roughest mode of life required little of decoration or ornament. The settlers were eminently practical too, even in the



Virginia, Maryland, and neighboring settlements. They neglected appearances as unconcernedly as the austere and self-mortifying Puritans of the New England colonies. So great was the prejudice against paint as a badge of worldliness and vanity in the Puritan settlements of New England in 1630 that a clergyman of Charlestown was actually brought before the council on charges of having paint about his dwelling. Forty years later an official list of mechanics and tradesmen disclosed that there was not a single painter in the Massachusetts Colony. Nevertheless, by 1714, painter's colors were for sale in Boston, and, although their use even for painting churches was frowned upon by the Puritans, the use of such colors by the wealthy grew slowly until the time of the Revolution.

In New York, whitewashed walls and woodwork painted a sort of bluish gray were quite general as early as 1748. Both there and in Philadelphia the use of paint increased far more rapidly than in New England.

By 1795, paint had become common. In the towns, the churches and public buildings showed the work of the painter, and even the ordinary householder used paint about his dwelling. If he was too poor to indulge in the luxury of an outside coat, the interior woodwork at least was painted. The white house with green blinds was then and for many years afterward the only type of ultra-esthetic decoration. The sole modification of this style was the use of a red paint in place of the more expensive white. Economy was the only reason for the red, however, and except for schoolhouses, churches where the congregation was very small, and homes where the people were poor, the white was always used.

During the period 1804 to 1820 white lead, red lead, and various-colored pigments, including Dutch pink, French green and blue, Prussian blues, and chrome yellow as manufactured in this country, became available.

By 1811, twenty-two different colors of paint were being made in Philadelphia. Tiemann states further that the first paints ready for use were made in 1852 by his house. They were tinted colors in paste form.

Bishop (7) records that in 1846 metallic zinc in a fine state of subdivision mingled with zinc oxide was ground in oil and used for paint upon the residence of Dr. Samuel Fowler at Franklin, New Jersey. This was the first application of zinc as a pigment. It preceded by several years the discoveries of Le Claire and Sorel in France, which were deemed of so much importance that these men received a large

pecuniary reward from the French government and were decorated with the cross of the Legion of Honor.

According to Heckel (35) prepared paint was unknown up to 1867. Colors in oil or even white lead in oil were not available much earlier. The slab and muller first and then the "Harris Mill" became regular items of paint shop equipment to which the older painters objected as strenuously as they did later to prepared paints.

The first prepared or ready-mixed paints are commonly accredited to one D. R. Averill, of Newburg, Ohio, who under date of July 16, 1867, patented a paint of this type and began its manufacture and sale. The claims under this patent show it to have been an "emulsion" enamel rather than a paint. In fact, the introduction of American process zinc oxide in 1852 more than anything else made the prepared paint industry possible.

Mineral paints were produced and sold as early as 1870. According to Heckel this type of paint was manufactured by his father. Straight linseed oil was used, and pure white lead was the base of the tints. The product was marketed as Heckel's Patented Silex Mineral Paint.

Painters, at first, refused to accept the ready-mixed paint. They preferred to mix their own product, following their own specifications. Accordingly, the manufacturers of prepared paint made only slight progress until about 1880. Then factories were established in such great numbers that within a decade or two their proprietors were forced to reach out for wider markets. Thus was ushered in an era of extraordinarily keen competition.

As reported by Job (41), the study of paints was given great impetus about the year 1890 through the published investigations of Dr. Charles B. Dudley, for many years the able, widely known, and respected chemist of the Pennsylvania Railroad. Much valuable information resulted from Dr. Dudley's work. In his studies, among other things, the properties of paint materials were systematically investigated, and what was learned brought about radical changes in the composition and manufacture of paints. It was clearly realized, for example, that the effectiveness of a paint did not by any means depend upon its cost per gallon or pound. It was proved that some of the most durable paints could be obtained at a minimum cost.

Other large corporations followed the lead of the Pennsylvania Railroad. The results of some of these investigations were presented by Job (42) before the Franklin Institute and elsewhere. The size and form of the particles of the pigment were shown to have a great influence upon the life of a paint coating, though this subject had not

previously received any attention. These tests demonstrated that some of the most durable paints were composed of the simplest and least expensive of pigments. This fact created a good deal of interest because the findings ran counter to the preconceived ideas of many who had assumed that in order to be really good and give long service a paint must be composed of one of the more expensive pigments, such as white lead, and that those which contained the so-called "inert materials" were to be looked upon as "doped" products. It became necessary because of these conditions to determine the truth about the properties and characteristics of the different paint materials. This work was finally undertaken by the Scientific Section of the Paint Manufacturers' Association of the United States.

Gardner (25) has written a detailed discussion of many of the tests conducted during this period, about 1906 to 1910. The more pertinent of these tests included a series of exposures on commercial paints carried out at the North Dakota Experimental Station; also test fence exposures at Atlantic City, New Jersey, and Pittsburgh, Pennsylvania.

According to Gardner the inspectors reached the unanimous conclusion that a paint made from any mixture of more than one white opaque pigment, either when used alone or in combination with small percentages of inert pigments, is far superior to any one single pigment paint. He further states that it was conclusively demonstrated that mixtures of white lead and zinc oxide, properly blended with moderate percentages of reinforcing pigments, such as magnesium silicate, barytes, silica, and calcium carbonate, are most satisfactory from every standpoint and are far superior to mixtures of prime white pigments not reinforced with extender pigments.

As recorded by Heckel (36), there were undoubtedly many test fences in use at this time, by individual manufacturers to evaluate their own as well as their competitors' paint products on a practical scale.

Other large-scale public test fences were constructed at Nashville, Tennessee, in 1910; Washington, D. C., in 1911; Arlington, Virginia, in 1912; and Manhattan, Kansas, in 1915. In general their result in regard to pigmentation agreed with the results reported for the earlier fences.

Vehicle information of interest was developed on the Washington fence as reported by Gardner (26) to the effect that linseed and perilla oils gave the most satisfactory results. Certain mixtures of these oils with soybean, lumbang, corn, cottonseed, and sunflower oils

also gave very good results. Boiled oils containing driers proved less durable than the same oils in the raw state. Blown and bodied oils increased the gloss of paints and did not detract materially from their durability unless an excess of thinner was used. Marine animal oils, when used in quantity, caused marked retention of dust and softening of film in damp weather. Treated tung oil caused cracking. Fixed petroleum oils proved unsatisfactory. Rosin oil caused disastrous effects when used in any percentage.

40/40/20-Lithopone/Zinc Oxide/Inert, as introduced in 1924 (52), was one of the earliest outside house paint composite pigment combinations promoted in the paint trade.

40/45/15-Lithopone/35% Leaded Zinc Oxide/Inert, better known as Formula "K," was first actively promoted in 1930 (43). This formula was well received in the industry and still commands a fair amount of consideration.

With the advent of reasonably priced titanium pigments, however, the trend of outside house paint pigmentations has been and still continues to be in the direction of titanium type paints. In other words, the constant desire of the paint manufacturer to produce outside house paints which have better durability and lower cost together with greater consumer satisfaction has led to a gradual evolution from lead in oil to lead-zinc, subsequently to lithopone, and finally to titanium type paints. It is true, however, that each of these various types of paints continues to be made and sold in sizable quantities. Nevertheless, the trend is more and more toward titanium type paints.

Protective coatings have been discussed in considerable detail by Carrick (17) and reference to his bulletin should be profitable for those interested in this subject.

### Composition

House paints as produced today generally consist of a composite of various pigments and extenders in linseed oil. Driers and thinners are used as required in order to achieve satisfactory application and performance characteristics.

**The pigments** most commonly encountered in house paints include basic carbonate white lead, basic sulfate white lead, zinc oxide, leaded zinc oxide, lithopone, zinc sulfide, and titanium dioxide. There are many grades and modifications of each of these pigments, and there is no question but that a change in grade or modification may have a very marked bearing on the properties of the resulting house paint. The various opaque and extended pigments are discussed in detail by

chapters in Volume II, each under its own name. Reference should be made to such chapters for further information regarding these pigments.

Broeker (10) has described the value of many of the common house paint pigmentations. Much of the following discussion is taken from his paper.

White lead in linseed oil has been considered for a long time by many as the one paint which is "foolproof." Its continued popularity is in large part due to the good repaint surface which it normally presents. White lead films, however, very rapidly acquire a heavy coating of dirt with resultant poor appearance. This heavy dirt collection persists for a considerable time, usually well into the second summer, when the film finally begins to chalk. The chalking and removal of the dirt coating are very irregular, with the result that the film presents a "splotchy" unsightly appearance for a still further period. Checking failure appears about the same time and rapidly takes on the characteristic "box effect." These checks gradually extend through to the wood as cracks. The film usually continues to show good adhesion to the wood and generally presents a fair repaint surface unless left for an abnormally long time before repainting. Naturally the life of the lead film is comparatively long, being assisted by the period of dirt collection as the film lies practically dormant until chalking commences. Tints of lead paints show fair fade resistance but exhibit the same characteristics of heavy dirt collection and failure as previously described.

Lead-zinc type paints (basic carbonate white lead-zinc oxide) have been very popular and widely distributed by paint manufacturers for a number of years. These paints act very similarly to lead in oil. They gradually acquire a heavy collection of dirt which persists for a considerable time, and when chalking starts uneven cleaning is often observed. Checking develops with chalking, and generally progresses to the cracking-flaking type failure. If the film is allowed to remain too long before repainting a comparatively poor repaint surface will result. The cracking-flaking failure becomes more rapid and more severe as the zinc oxide content is increased. Tint retention is slightly superior to that of lead paints because of the harder film produced by the zinc oxide.

Lead-leaded zinc type paints are modifications of the lead-zinc paints previously described, 35 per cent leaded zinc oxide being introduced in place of the lead-free zinc oxide. These paints represent an improvement in the types of failure and repaint surface but are also

open to the objections of heavy initial dirt collection and poor general appearance for a considerable period of time after application. These general characteristics and values might roughly be classed with those of the lead in oil paints.

Lithopone and zinc sulfide in proper combinations with 35 per cent leaded zinc oxide and extenders can be used to produce paints which show good durabilities, retain good appearance throughout the lives of the paints, and produce good repaint surfaces. Lithopone and zinc sulfide are cracking type pigments, but, when they are used within the preferred compositional ranges, the degree of cracking failure can be controlled to some extent so that the films will fail more by erosion and thus present good surfaces for repainting when such treatment is desired or necessary. The lithopone and zinc sulfide type paints show comparatively good fade resistance, being somewhat superior in this respect to lead and lead-zinc type paints.

Titanium dioxide, in proper combinations with 35 per cent leaded zinc oxide and extenders, which is the latest stage of house paint evolution, gives still further improvements in hiding power, whiteness, and freedom from dirt collection, with still better durability than is exhibited by the lithopone paints (67). The unusual cleanness of the titanium type paints is a result of the inherent self-cleaning characteristic of these films. Properly formulated titanium type paints give excellent durability and a clean white appearance under normal conditions of exposure. Ultimate failure is by slow chalking and erosion, which leave an excellent surface for repaint work. These advantages are coupled with markedly superior hiding power because of the high refractive index of titanium dioxide.

The use of white titanium dioxide in tinted outside house paints has not been feasible until recently because of excessive fading. Special white titanium dioxide pigments are now available. These show inherently slower chalking and greatly improved tint retention properties; yet they retain, to a marked degree, the self-cleaning and excellent durability characteristics generally associated with titanium type pigments.

High opacity rutile titanium pigments were made available during the early part of 1941. Anderson (2) gives many pertinent properties of the extended rutile pigments, while Dawson (20) discusses both pure and extended rutile pigments as used in various interior and exterior finishes. These new rutile pigments possess such marked advantages in hiding power over the older anatase pigments that their value in modern finishes cannot be overlooked. Furthermore, there is an excel-

lent possibility that house paints of superior durability and performance can be made with these new rutile pigments.

Zinc oxide and leaded zinc oxide may best be looked upon as modifying rather than prime pigments. They are used in conjunction with various other pigments in order to control such factors as dirt collection, chalking, fading, and mildew (49). Recent developments in these pigments which are of importance in house paint formulation, because of ultimate durability effects, include the production of acicular particles (24) and the elimination of colloidal fines (23).

Selected extenders are used to obtain improved durability as well as to reduce costs. It seems established (44) that extenders such as mica, talc, magnesium silicate, and diatomaceous silica offer definite durability advantages over other extenders such as barytes, whiting, china clay, calcium sulfate, and ground silica. In selecting an extender, however, such factors as availability, color, fineness, and cost must be considered. When this is done certain types of magnesium silicate are found to possess outstanding all-round merit. In certain instances, however, where tint retention is important, whiting and calcium sulfate deserve consideration. Further details regarding various extenders can be obtained from Chapters 17 and 18, Volume II.

Combinations of certain of the prime and modifying pigments listed, together with selected extenders, constitute the pigmentation of most of the better grades of ready-mixed outside house paints. Figure 1 shows a triangular graph of these constituents. It is similar to the one presented by Broeker (11) in his paper on exterior paints and will serve to show in a simple way the compositional ranges for some of the more promising pigmentations used in house paint formulation.

Points within the area shown in the center of the graph represent the pigment compositions generally considered most desirable. It should be noted that these pigment combinations cover a range of 30 to 50 per cent for the prime pigments, 30 to 50 per cent for the modifying pigments, and 10 to 30 per cent for the extenders. These compositions for the most part give paints which are resistant to such failures as mildew, early cracking, and excessive chalking.

A graph of this type can be used as a guide in designing systematic studies of various pigmentations. The following example will serve as an illustration.

*Example.* Where a titanium magnesium pigment/leaded zinc oxide/extender pigmentation is to be studied, reference to the graph will show a wide range of compositions which deserve consideration. The center of the preferred compositional ranges is indicated by 40 per

cent titanium magnesium pigment, 40 per cent leaded zinc oxide, and 20 per cent inert. Other compositions indicated by the graph as of possible value are within the limits of plus or minus 10 per cent of each constituent. Under such conditions the actual titanium dioxide content of the pigmentations selected would range from 9 to 15 per cent.

Leaded zinc contents below 40 per cent should be carefully evaluated for mildew and erosion resistance. It should be recognized, of

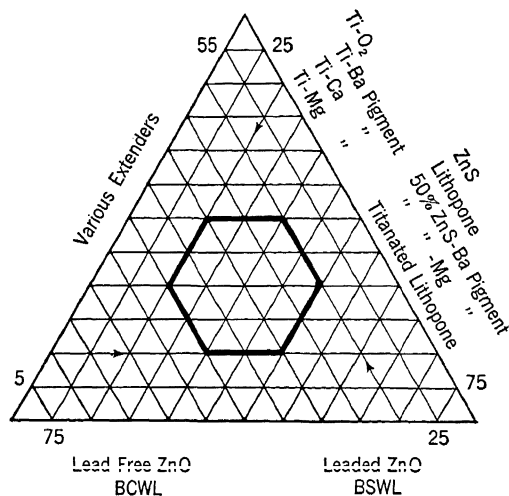


FIG. 1.

course, that hiding power will be increased with increasing amounts of prime pigment and that in certain cases, depending on the opacity requirements, the preferred compositional ranges included by this graph would be inadequate. Should this occur, another graph covering the desired ranges of pigmentation should be designed.

Considering the wide variety and types of pigments and extenders, also the possibility of substituting basic carbonate white lead, basic sulfate white lead, and zinc oxide for the leaded zinc, one can readily see that a very large number of paints can be formulated within such preferred ranges.

In house paints the volume relationships of pigment to binder are really more pertinent than the weight relationships. Actually the pigment volume calculated on the non-volatile portion of the paint may vary over relatively wide limits without serious effects. Generally pigment volumes of about 28 to 30 per cent are considered most ac-



ceptable because of the fact that high pigment volumes tend toward excessive chalking, which results in rapid failure by erosion, whereas low pigment volumes give more dirt collection and mildew and tend toward plastic checking or an "alligator" type of cracking.

The binder commonly used in house paints is composed of linseed oil. A combination of 92 per cent alkali refined linseed oil and 8 per cent kettle-bodied linseed oil, body "Q" \* (4.35 poises), is popular and is known to give good results. The bodied oil is added to obtain improved durability. The amount of bodied oil which can be used to advantage is somewhat limited because of the fact that linseed oil bodied beyond "Q" or the use of larger amounts of "Q" bodied linseed both lead to poorer brushing characteristics.

It is recognized that acid refined linseed oil is used to a considerable extent, but its use should be surrounded by sufficient precautions to assure a fairly low and constant acid number in order to secure uniform consistency and avoid the possibility of granulation in the paint on aging. These precautions are particularly important if reactive materials are present in the pigmentation because of the danger of the formation of excessive amounts of metallic soaps. These same comments may well be applied to raw linseed oil, which is commonly used in the place of refined linseed oil in tinted or colored exterior house paints.

In recent years some house paints have carried tung (China wood) oil, perilla oil, soybean oil, or fish oil in various combinations with and without linseed oil. According to Holley (38) it can be definitely stated, on the basis of exposure results over the past ten years, that soybean oil has at least equal exterior durability and in numerous instances superior durability to linseed oil provided—and this is of the utmost importance—that an immediate, firm, non-plastic film be obtained. Otherwise durability is inferior to linseed oil and frequently unsatisfactory. In practice, soybean oil is normally diluted a great deal with linseed oil to give proper hardness. Dehydrated castor oil offers promise in exterior finishes because of its superior elasticity and water resistance characteristics as compared with linseed oil. Considerable information on this subject is given in the chapter on dehydrated castor oil in Volume I.

Also in recent years some house paints have been produced with a binder composed of linseed oil fortified by the addition of 5 to 10 per cent of resin, based on the non-volatile vehicle. This resin is ordi-

\* Gardner-Holdt scale.

narily introduced as a short-oil varnish. Granting that further improvements may yet be made, sufficient information on resin-fortified systems is available to justify a statement to the effect that such vehicles with zincless pigmentations generally show excellent durability, but in many localities they show excessive mildew and dirt collection. Furthermore, if zinc oxide is included in the pigmentation in sufficient amounts to give protection from mildew and prevent excessive dirt collection, excessive checking and cracking failure may be an undesirable result.

Although considerable work has been done in modern times with newer types of paints based on the use of various oils with or without resin fortification, the actual results available are limited and meager as compared with the exhaustive data accumulated on linseed oil type house paints during the last half century.

**Driers** are required in outside house paints to set or harden the oil in the paint film so that it will not collect dust or dirt and, furthermore, so that it will withstand abrasion. For this purpose lead and manganese linolate or naphthenate driers are generally used to the extent of about 0.6 per cent lead as metal and 0.02 per cent manganese as metal, calculated on the non-volatile vehicle in the paint.

Cobalt is of doubtful value as a drier in outside house paint and accordingly is often omitted. Although this point does not appear to be definitely proved, there are indications that cobalt driers promote early chalking and fading. Furthermore, there are some indications that cobalt driers accentuate checking failure, particularly in paints which do not have good resistance to checking and cracking.

As compared to naphthenate driers, linoleate driers give essentially equal durability. When used in most outside house paint systems, linoleate driers contribute better mixing and wetting properties than naphthenate driers. In fact, 1 to 1 paste paints, that is paste made to blend 1 volume of paste paint to 1 volume of linseed oil to give a ready-mixed paint satisfactory for application, can generally be mixed and ground with very little difficulty when linoleate type driers are used, whereas, with naphthenate driers added to give the same metal content, the mixes are usually too stiff to handle without some further reformulation. Linoleate driers, too, cause more false body than naphthenate driers. Thus, linoleate driers permit a higher thinner content with an accordingly lower cost per gallon of paint. They also yield better brushing together with slightly poorer leveling and slightly poorer gloss.

**Thinners** are used in outside house paints to bring the paint to a good working consistency. Mineral thinner of a boiling range of 150 to 215° C. is normally used in place of turpentine because it gives fully as good results at a lower cost. The amount used may range from 0 to 20 per cent by volume. This thinner content is important. Obviously, high thinner contents contribute to low costs, high spreading rates, and thin films. All these factors are sufficiently important to deserve very careful consideration.

**Tinted outside house paints** are of course very common. For the most part these paints are made from lead-zinc, lithopone, zinc sulfide, or chalk-resistant titanium type base paints. White lead and regular titanium pigments are not used to any great extent in tinted exterior paints because of excessive fading. A careful selection of tinting colors is necessary to assure that outside house paints will have good tint retention. Generally, earth colors are considered most satisfactory. Other widely used tinting colors include chrome green, hydrated chromium oxide, phthalocyanine green, chrome yellow, ultramarine blue, iron blue, phthalocyanine blue, and lampblack. Organic colors, for the most part, are not sufficiently permanent and are, therefore, of doubtful value.

### Preparation

The essential steps in the preparation of exterior house paints include mixing, grinding, thinning, and tinting. Long (45) has published a detailed account of each of these operations, and much of the following discussion is taken from his paper.

The **mixing operation** which is required previous to grinding on a burrstone mill or roller mill is generally considered very important. Besides being a cost factor which must be considered it may have far-reaching effects on quality. The primary purpose of the mixing operation is to distribute the ingredients into a uniform paste and to wet the pigments with the vehicle as thoroughly as possible. Too often the time of mixing is inadequate to wet the pigments completely by the vehicle, or the vehicle used in the operation is not a sufficiently good wetting vehicle to thoroughly wet the various pigments; consequently, unwetted agglomerates remain after the mixing operation is terminated and these are often incompletely dispersed in the subsequent mill grinding operation. Accordingly, it should be emphasized that mixing should be continued until the paste has become quite uniform. Where it is necessary to make a mix with limited amounts of vehicle and where the vehicle is very poor in wetting properties, it

is often advantageous to sweat the mixed paste overnight before attempting to make the grind.

In making a mix, the usual practice is to place the vehicle to be used in the mixer first. The pigments are then added rapidly until a stiff paste is developed and then slowly, maintaining a stiff but pasty mass throughout the entire operation. Too rapid addition of the pigment may result in balling in the mixer, which will place excessive strain on the equipment and cause excessive power consumption. Sufficient mixing time should be allowed after all the pigment is added to insure a uniform paste. It is good practice, too, where the formula permits, as is usually the case with outside house paints, to make and keep the paste relatively stiff throughout the mixing time and to add such additional vehicle as is needed to give a satisfactory milling paste just previous to the grinding operation. The shearing action which can be developed in a stiff paste is a very decided help in breaking up the large unwetted lumps of pigment which are so often encountered in the mixing operation.

**Grinding** usually means dispersing rather than a reduction in size of the individual pigment particles. In the case of some earth pigments and extenders the fundamental unit particle of the pigment is broken up into fragments by the mills. Thus, the pigment actually is ground up finer although the unit pigment particles of most chemical colors are already fine enough. However, in the process of manufacture, especially in drying and during shipment and storage, these minute pigment particles agglomerate to some extent into clusters which constitute larger particles. Good mixing serves to disperse these clusters to a considerable degree but generally not sufficiently completely. Consequently, when the pigment and vehicle have been thoroughly mixed and are seemingly well wet, it is still necessary to pass this mixture through some kind of mill to rub apart these clusters within the vehicle, with the expectation that the fresh surfaces exposed by this rubbing action will be promptly wet by the vehicle and that the individual particles will thus be permanently separated by the vehicle. Actually, the various mills or devices used to "grind" paints are not perfect so that even after the well-mixed material has passed through the mill there are still some agglomerates not perfectly broken up. Particles that have been dispersed and wet may gather together again, thus resulting in a condition generally known as flocculation.

The fineness of a paint grind is often judged in a preliminary way by rubbing the paste with a spatula on a smooth surface such as a glass plate. The extent of the striations produced by this procedure

is a rough measure of fineness. In making this test, however, care should be taken to prevent excessive working of the paste with the spatula which in itself would be an effective grinding operation. Standards are often helpful in making such fineness ratings.

The common devices used to grind or complete the dispersion of the pigments in the vehicle are burrstone mills, roller mills, and pebble or steel ball mills. Previously mixed pastes are fed either to the burrstone mill or to the roller mill, and in most cases the mill is adjusted to give the desired fineness or dispersion. If, however, the paint is not sufficiently fine after passing through the mill it can be reground. A second grind on outside house paints is seldom necessary, however, because the fineness requirements for such paints are not particularly severe.

In the pebble or ball mill the mixing and grinding are carried out as one operation. The vehicle and pigment are charged directly into the mill in amounts known to give a satisfactory grinding consistency in this type of mill. Fineness is controlled by pebble or ball paste ratios and by grinding time. Other factors being equal, the higher the ball or pebble paste ratio by weight the finer the grind.

Of these various types of grinding equipment the burrstone mill or the roller mill must be used when heavy pastes are to be ground. The roller mill will undoubtedly handle heavier pastes than the burrstone and will show its greatest value on pastes which require relatively little work in the grinding operation. Where considerable work must be done in the grinding operation, particularly on very hard pigments such as silicates, silica, iron oxides, ochers, and sienna, the burrstone mill or pebble or ball mill should be used because of the abrasive action of such pigments on roller mills. Where relatively thin grinding pastes are permissible and where relatively large batches are involved the pebble mill shows its maximum advantage, and the more difficult the grind the greater this advantage. For further details on this important operation, the reader should see Chapter 2, Volume IV.

**Thinning and tinting**, if desired, follow the grinding operation. The ground paste is mixed with the remaining quantities of oils, varnishes, driers, thinners, and any other liquids to be included, but no dry pigments are added. Mixing and stirring are continued as required to obtain a uniform mass. It is generally accepted as best practice to cut the paste consistency gradually with continued stirring as such a procedure materially aids in obtaining good dispersion of the paste paint.

If tinting is to be done the colors previously ground in oil are mixed with limited amounts of the batch to be tinted and then added directly to the batch and the whole stirred until the colors are uniformly distributed. Care must be taken to avoid adding so much tinting color that the product becomes too dark even though it is otherwise the right combination. The tinter must have an eye for color to judge what to add to modify the shade in the proper direction. Tinting is therefore something of an expert craft and requires considerable time and effort.

After the batch has been tinted and thinned to the proper extent, it is strained and poured into cans. For further details, the reader should see Chapter 24.

### Testing

**Physical tests**, which are generally made on outside house paints, include consistency, gallon weight, brushing, drying, leveling, fineness, gloss, color, and hiding. Gardner (27) has written excellent detailed accounts of the various methods which can be used in making each of these tests, and this reference should be consulted regarding any

problems which may be encountered in connection with such work. Relatively simple and rapid tests can be made on house paints, which will be, in most cases, entirely sufficient and satisfactory.

Consistency can be easily and quickly determined by using the Krebs modification of the Stormer Viscometer. By means of this instrument consistency is given a numerical rating in terms of the weight required to give 200 revolutions per minute for a standard paddle immersed a given distance in a paint under constant temperature conditions of  $25^{\circ}\text{C.} \pm 0.5^{\circ}\text{C.}$  ( $77^{\circ}\text{F.}$ ). Although such consistency measurements do not necessarily measure the extent of a puff or false body, they are a very useful aid in the duplication of a given paint. The ease and rapidity with which these readings can be made give this method of consistency control a very definite advantage over various

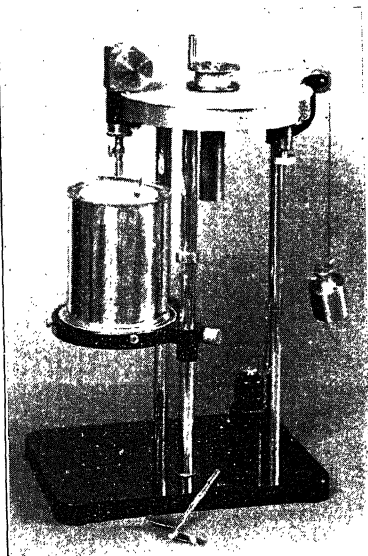


FIG. 2. Krebs Modified Stormer Viscometer.

TABLE I  
STORMER CONSISTENCY  
TIME-WEIGHT

Grams	75	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	1,000	1,100	1,200	1,300	1,400	
Sec.	Consistency																							
24	42	52	65	75	83	90	95	99	103	108	111	115	118	122	125	128	130	132	136	138	139	141	142	
25	45	54	66	76	84	90	95	100	104	109	112	116	119	122	125	129	131	133	137	138	140	141	143	
26	47	56	68	78	85	91	96	101	105	110	113	117	120	123	126	130	132	134	138	139	141	142	144	
27	49	57	69	79	86	92	97	102	106	111	114	118	121	124	127	130	132	134	138	140	141	143	144	
28	51	59	70	80	87	93	98	102	107	112	115	118	121	124	127	130	132	134	139	140	142	143	145	
29	53	60	71	81	88	94	99	103	107	112	115	119	122	125	128	131	133	135	139	141	142	143	145	
30	54	61	72	82	89	95	100	104	108	112	116	120	122	125	128	131	134	136	140	141	143	144	146	
31	55	62	73	82	90	95	100	104	108	113	116	120	123	126	129	132	134	136	140	142	143	145	146	
32	56	63	74	83	90	96	101	105	109	113	116	120	123	126	129	132	134	136	140	142	143	145	146	
33	57	64	75	84	91	96	101	105	109	114	117	121	123	126	129	132	135	137	141	143	144	145	147	
34	58	64	75	84	91	97	102	106	110	114	118	122	124	127	130	132	135	137	141	143	144	146	147	
35	59	65	76	85	92	98	102	106	110	114	118	122	124	127	130	133	135	137	142	143	145	146	148	
36	60	66	76	85	92	98	103	107	111	115	118	122	125	128	130	133	135	137	142	144	145	147	148	
37	61	67	77	86	93	99	103	107	111	115	119	123	125	128	131	133	136	138	142	144	145	147	148	
38	62	68	78	87	93	99	104	108	112	116	119	123	126	129	131	134	136	138	142	144	145	147	148	
39	62	68	78	88	94	100	104	108	112	116	120	124	126	129	131	134	136	138	143	145	146	148	149	
40	63	69	79	88	94	100	104	108	112	116	120	124	127	130	132	134	136	138	143	145	146	148	149	

other more laborious procedures. Figure 2 is a picture of a Krebs modified Stormer Viscometer fitted with a fork type paddle. The figure also shows a more recent blade type paddle which appears to have some advantage over the older fork type in that it is less sensitive to variations in depth of immersion.

This method of rating consistency is discussed in considerable detail by Valentine and MacLean (68). This reference should be consulted for a more complete discussion of the various factors involved. Table I is an empirical time-weight chart in which 100 represents the consistency of a medium-bodied paint. The usual types of ready-mixed paints seldom run thicker than 140 or thinner than 60. To measure the consistency, the can of paint is brought to the proper temperature, thoroughly stirred to make sure that all pigment is in suspension, and placed on the stand of the instrument. The stand is then raised until the surface of the paint in the container rises to the marks on the fork or blade type paddle. Weights are attached to the cord on the stormer and adjusted until the time reading falls between 24 and 36 seconds, preferably at 30 seconds per 100 revolutions of the paddle (200 rpm). This time in seconds is then located in the first vertical column of the chart and translated into consistency by crossing horizontally to the vertical column headed by the weight in grams used in obtaining the time reading.

Repeated house paint tests have indicated that the most practical and acceptable consistency range is 80 to 90 Stormer units. In order to take care of special conditions, house paint is frequently applied with entire satisfaction at consistencies of 100 to 125 Stormer units. Consistency, however, does not measure durability and any tendency to pick thick paints in preference to thin paints because of the possibility of adding extra oil or thinner before application cannot be commended.

Geddes and Dawson (32) have shown how the yield value and mobility of various paint systems can be determined by means of the modified Stormer Viscometer. Such determinations make it possible to define a paint system more accurately. It is pointed out that an increase in yield value means an increase in false body and poorer leveling, whereas an increase in mobility indicates improved brushing.

The Gardner Mobilometer is another instrument which is widely used to determine paint consistency. It is very simple to operate, and a number of determinations may be run in a very short time. Figure 3 is a picture of a Gardner Mobilometer. As described by Gardner (27), this instrument consists essentially of a cylinder supported by



a base plate, a plunger or piston, and a bracket to support the plunger. The plunger consists of a disk with 51 perforations  $\frac{1}{16}$  inch (1.59 mm.) in diameter and a weight pan attached to the end of a brass tube. Two supplementary disks, which greatly extend its range, are supplied with the instrument. One is solid; the other has four holes 6.25 mm. in diameter.

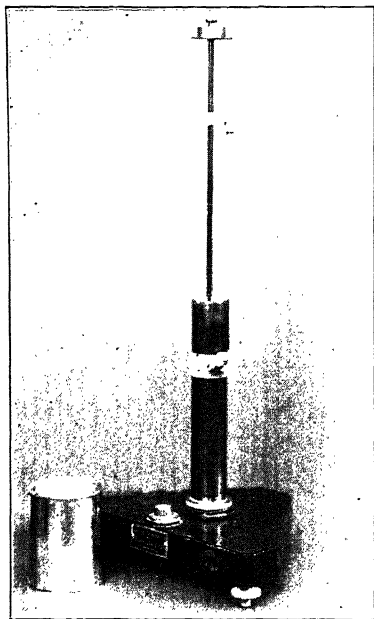


Fig. 3. Gardner Mobilometer.

The weight of the moving system which includes the disk, connecting tube, weight pan, and lead shot in the hollow connecting tube is 100 grams. (This is not the case with Gardner Mobilometers distributed prior to September, 1931.)

The cylinder is filled to a depth of 20 cm. with the material to be tested. The cylinder is leveled by means of the adjusting screws. The disk end of the plunger is then introduced into the cylinder and the bracket attached. The time required for two marks 10 cm. apart on the stem of the plunger to pass through the collar is then recorded. Some operators may prefer to use a greater length of travel. This is done by making the required marks on the stem. The marks have previously been located

so that they pass through the collar of the bracket as the disk passes through the mid portion of the cylinder. Thus the plunger is in motion both at the beginning and the end of this interval. There may be slight variations in individual Mobilometers. In order, therefore, to bring all values to a common basis, the Gardner Mobilometers are calibrated in terms of a master instrument. It is necessary, however, to employ this factor only when making accurate determinations of a fundamental nature. Thus if a correction factor of 1.038 is issued with a mobilometer, it will be necessary to multiply the seconds by this figure, unless approximate results only are required. Typical data obtained with a mobilometer are given in Table II. Unless the temperature is definitely specified in a report it is understood that all determinations have been made at  $25^{\circ}\text{C.} \pm 0.5^{\circ}\text{C.}$  ( $77^{\circ}\text{F.}$ ).

TABLE II

MOBILITY DETERMINATIONS AT 25° C.

(Time in seconds for the plunger to fall through 10 cm. of exterior house paint, using disk with 51 holes)

<i>Total Load—Grams</i>	<i>Seconds</i>
100	24.7
150	13.5
200	9.1
250	6.9
300	5.5
Load of 186	for 10

One method of evaluating the data obtained with the mobilometer is to plot the total load against the reciprocal of the time. This is equivalent to plotting speed in decimeters per second against the load.

The results may be expressed also as the load required to cause the plunger to descend at the rate of, say, 1 cm. per second. It is not necessary to obtain this value directly. For example, consider the house paint in the table. A load of 150 grams on the plunger caused it to descend in 13.5 seconds, a load of 200 in 9.1 seconds. By simple interpolation, the load for 10 seconds is

$$200 - \frac{10 - 9.1}{13.5 - 9.1} \times 50 = 190$$

It is, of course, more accurate to plot the data and obtain the value directly from the curve. This is the manner in which the load for 10 seconds was determined in Table II.

Another method expresses the results as the product of the time and load divided by the distance traveled. For viscous materials the expression will be a constant as in the following formula:

$$K = \frac{L \times t}{d}$$

where  $K$  is a constant,  $L$  the total load in grams,  $t$  the time in seconds, and  $d$  the distance in centimeters.

Weight per gallon can be obtained readily by a determination of the weight of paint required to fill a cup which is designed to contain exactly 83.3 grams of water. The weight in grams of the paint in the cup divided by 10 gives the weight in pounds per gallon of

paint. The weight in grams multiplied by 0.012 gives the specific gravity. Figure 4 is a picture of such a cup. The inside of the cup is rounded at the bottom to facilitate cleaning. When in use, paint is added until the cup is almost full. The cover is then put in place and the excess paint wiped off.

Contrary to much advertising on the subject, weight per gallon does not determine the quality or durability of a paint.

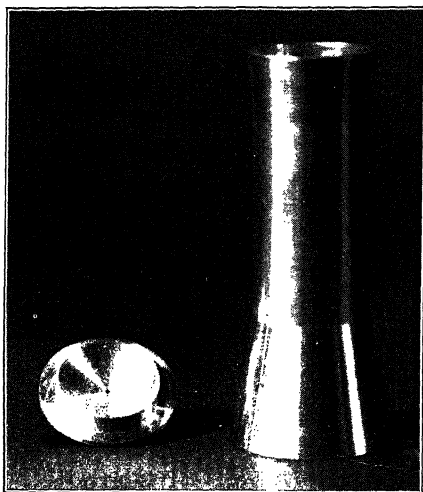


FIG. 4. Du Pont Gallon Weight Cup.

Brushing, drying, leveling, fineness, gloss, color, and hiding can all be determined by making brushouts in comparison with known standards on hiding power charts, of which there are many different types. Black striped beaver boards of a convenient size can also be used.

It is better to determine brushing in a practical way, however, by making brushouts against known standards on a relatively large area, where it is possible to use a three-inch brush with a normal brushing stroke. The use of a large area for such tests is important if reasonably accurate ratings are to be obtained. A certain tooth is sometimes desired, and it is often a matter of opinion as to just what constitutes a good brushing paint. Generally speaking, however, a house paint with a slight false body or puffy type of consistency is preferred to a paint which flows and runs readily because this latter type of paint is liable to give excessive splattering or run down the brush handle, thereby making a neat, clean-cut paint job difficult.

The drying characteristics of an outside house paint are usually considered satisfactory if the film is reasonably dry on overnight exposure. The tendency in house paints is to use as little drier as will give a satisfactory overnight dry. The drying time of a given paint is not always constant and is changed by variations in temperature, humidity, ventilation, etc. Actually, in cold weather, it may be necessary to double the drier content in order to approximate normal drying. Also under severe temperature conditions an additional amount of manganese drier is often helpful. In such cases the driers may be used in amounts as high as 1.2 per cent lead as metal and 0.06 per cent manganese as metal, calculated on the non-volatile of the vehicle in the paint. When the temperature is so low that the thinner will not evaporate, the drying characteristics undoubtedly will be rather unsatisfactory even with additional drier. Painting should certainly not be undertaken under such conditions.

Leveling, fineness, and gloss are best judged from brushouts. Although there is a tendency on the part of the consumer to demand excellent leveling and fineness as well as a high gloss, certainly these properties have to do for the most part with the initial appearance rather than the ultimate appearance or durability of the paint. Generally those formula changes which lead toward better leveling and higher gloss such as the addition of varnish or the use of larger amounts of bodied oil lead also toward poorer durability or poorer brushing characteristics. Accordingly, such changes if made at all should be made with considerable caution.

Color and hiding power often can be judged advantageously by making drawdowns with a doctor blade on hiding power charts and comparing them with accepted standards. Although some circumspection must be exercised in the interpretation of such results (51), there is little doubt that such easy and quick tests are of considerable value.

**Exposure tests** on outside house paints have been accepted for a number of years as a prerequisite for intelligent house paint formulation. Experience has indicated that the more rapid or accelerated the exposure test, the less reliable the results. This means that house paint exposure tests as made in more recent times are for the most part confined to south and north vertical test fences, coupled with actual house test comparisons for those paints which appear to be most promising.

Southern exposures at 45° are used to some extent even today for accelerated results on dirt collection, chalking, fading, and durability.

However, such results are discounted to a considerable degree because they often do not agree with actual house test results. Furthermore, there are indications that such accelerated tests may fail entirely in showing paint film differences which may be exceedingly important. This is especially true with relation to fading, dirt collection, and mildew characteristics. There are indications, too, that marked differences in dirt collection so often encountered between 45° south and south vertical exposures affect in turn durability as governed by chalking, checking, and cracking type failures.

In making test fence exposures, a very definite effort should be exerted to eliminate unnecessary variables. A reasonable practice, which has been tried with acceptable results, is described as follows:


The panels which are used in making the exposure tests, except in instances where the studies involve various woods, should be carefully selected to eliminate knots, pitch, etc. Edge grain white pine or cedar is normally used. Wood failures can be eliminated to some extent if the panels are painted on the backs and edges with a good protective coating prior to the application of the test paint to the front of the panel. If the panels are not backed, the test is more severe. Accordingly, the procedure adopted should be kept uniform.

In applying the test paints, a regular painting schedule should be followed as closely as possible, allowing a suitable fixed drying period between the first and second coats, and between the second and top coats. Drying periods usually range from two to seven days. The panels should be placed on the fence as soon as possible after the third coat is dry.

The exposed panels should be inspected periodically, generally at three-month intervals. Particular attention should be paid to such paint film changes as dirt collection, gloss, chalking, checking (including microscopic checking), cracking, flaking, erosion, mildew, and general appearance. Screen staining tests can be made readily if desired. In tinted paints, special consideration is given to tint retention. The progress of each paint throughout the life of the film can be followed readily by means of charted data. The final observation is directed generally to the type of surface left for repainting after the failure of the original paint. Figure 5 shows a record sheet for charting such data, as approved by the Federation of Paint and Varnish Production Clubs.

### EXPOSURE RECORD

Test No.

Problem No. _____		Paint No. _____ Color _____	
General Purpose of Test: _____		<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">             Pigment   </div> <div style="text-align: center;">             Pig.   Bind.   Volatile              _____           </div> </div>	
Inspected By _____		Vehicle _____ Pigment Vol. _____	
Exposed _____	Removed _____	Filed _____	

		GENERAL APPEARANCE																COLOR															
		0	3	6	9	12	15	18	21	24	27	30	33	36	0	3	6	9	12	15	18	21	24	27	30	33	36						
Pl	10																																
G	9																																
I	8																																
Pr	7																																
PCC	6																																

		GLOSS																															
		0	3	6	9	12	15	18	21	24	27	30	33	36	0	3	6	9	12	15	18	21	24	27	30	33	36						
Pl	10																																
G	9																																
I	8																																
Pr	7																																
PCC	6																																

		CHALKING																CHECKING															
		0	3	6	9	12	15	18	21	24	27	30	33	36	0	3	6	9	12	15	18	21	24	27	30	33	36						
Ab	10																																
S	9																																
I	8																																
B	7																																
CF	6																																

		CRACKING																FLAKING															
		0	3	6	9	12	15	18	21	24	27	30	33	36	0	3	6	9	12	15	18	21	24	27	30	33	36						
Ab	10																																
S	9																																
I	8																																
B	7																																
CF	6																																

		SCALING																BLISTERING															
		0	3	6	9	12	15	18	21	24	27	30	33	36	0	3	6	9	12	15	18	21	24	27	30	33	36						
Ab	10																																
S	9																																
I	8																																
B	7																																
CF	6																																

		PEELING																RUSTING															
		0	3	6	9	12	15	18	21	24	27	30	33	36	0	3	6	9	12	15	18	21	24	27	30	33	36						
Ab	10																																
S	9																																
I	8																																
B	7																																
CF	6																																

Pl-Perfect	G-Good	I-Intermediate	Pr-Poor	PCC-Poorest Cond. Conceivable	Ab-Absent	S-Slight	B-Bad	CF-Comp Failure
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Notes \_\_\_\_\_

EXPOSURE AND PAINTING DETAIL

Location \_\_\_\_\_

Atmospheric Condition: Rural \_\_\_\_\_ Urban \_\_\_\_\_ Industrial \_\_\_\_\_

Type \_\_\_\_\_

Facing: North \_\_\_\_\_ South \_\_\_\_\_ East \_\_\_\_\_ West \_\_\_\_\_ Vertical \_\_\_\_\_ 45° \_\_\_\_\_

Material Painted \_\_\_\_\_ New \_\_\_\_\_ Repaint \_\_\_\_\_

Condition and Preparation of Surface \_\_\_\_\_

Protection of Back \_\_\_\_\_

Application Method { 1st Coat \_\_\_\_\_

and { 2nd Coat \_\_\_\_\_

Drying Conditions { Finish Coat \_\_\_\_\_

SECOND SHEET OF THE FEDERATION OF PAINT & VARNISH PRODUCTION CLUBS

FIG. 5.

Naturally certain combinations of materials give more promising results than others. These more promising paints should be subjected to additional tests by actually painting houses with them. The houses selected for test purposes are usually of the clapboard type. In each case a definite attempt should be made to obtain information regarding the paints previously used on the house.

The paints as supplied for these test houses should be reduced and ready for application. Control paints should be supplied with the test paint in order to determine the value of the test paint in comparison with other well-known paints.

When the paints are delivered for a house test, it is well to make appointments with the home owner and the painter so that satisfactory locations for the controls can be selected and diagramed. The controls are preferably located in an open southern exposure sufficiently low to permit a close examination. The painter should be cautioned to use the paints as supplied without making adjustments of any kind. He should be further cautioned to clean his brush or, preferably, use a different clean brush when changing from the test paint to the control paint in order to prevent contamination of one paint with another. The painter should be requested to make sharp lines of demarcation between the test and the control paints and to be careful not to brush one paint into the other. He should be further requested to refrain from painting during wet weather. The painter should be asked to judge the merits and faults of each paint and to rate the paints in order of preference.

Generally the painter is not told the composition of the paints until after he has completed and reported his ratings. This often proves very helpful especially in cases where the painter has a special fancy for some particular brand of paint. Sometimes he is surprised to learn that he has picked another paint as superior to his favorite.

As in the case of the panels on the test fences, the paints on these test houses should be inspected at regular intervals and records made of the condition of the paint on each side of the house, paying particular attention to comparisons between the test and the control paints when subjected to the same exposure conditions.

Differences in such properties as dirt collection in protected areas, resistance to moisture failure, and screen staining are observations which can be made on test houses much more readily than on test fences.

Climatic conditions have undoubtedly a marked effect on the type and rapidity of failure encountered with various outside house paints.

Marshall, Iliff, and Young (48) show temperature and humidity variations at Miami, Florida; Philadelphia, Pennsylvania; and Amarillo, Texas; as follows:

	MIAMI	PHILADELPHIA	AMARILLO
Max. temp. variation—Daily .....	24	42	65
“ “ “ —Two-week period .....	35	46	78
“ “ “ —For one month .....	38	58	82
Temp. variation for entire year .....	49	96	112
Max. humidity variation—Daily .....	53	39	71
“ “ “ —Two-week period .....	63	70	83
“ “ “ —For one month .....	27	21	55
Max. ave. humidity variation for year 1933 .....	27	32	58

From extensive exposures made at these three locations, conclusions are drawn to the effect that

1. Miami exposure favors the less flexible hard film types of paint. These generally receive a better relative rating in any series at Miami than at the other exposure stations. Amarillo exposure, on the other hand, causes rapid failure of the less flexible hard film types. They generally receive a lower relative rating in any series at Amarillo. In the vicinity of Wilmington, intermediate results are secured. Here film hardness appears to have less effect on ultimate film integrity.

2. Tests in one locality cannot be accepted as a criterion of paint performance for the country as a whole. For example, it is unsound practice to base the general recommendation of a paint for wood upon results of Florida tests, even perhaps when supplemented by results in a climate such as that of Wilmington.

Broeker (10) states that, owing to the prevailing higher temperatures in the southern states, a greater flexibility of paint films is obtained with formulas which, on northern exposure, might show film rupture due to lower temperatures and more rapid temperature changes. In all the southern states, there is a high concentration of ultraviolet light which is more accentuated in the southern portion of a narrow coastal strip. This condition leads to more pronounced chalking of the films, and the paints must therefore be formulated to compensate for this factor. High humidity is prevalent throughout the coastal area, and this condition induces mildew and mold growth. This factor must also receive consideration when formulating an exterior paint.

From the foregoing, it can be seen that panel tests and house tests at various locations in the country which represent widely differing



climatic conditions are needed in order to evaluate thoroughly any relatively good exterior paint.

**Accelerated tests** on exterior paints have received a great deal of attention by investigators in the paint industry. Reports (4) indicate that, although a considerable amount of such work has been done and a number of promising leads obtained, no generally satisfactory accelerated testing procedure for exterior paint has yet been found. As a matter of fact, although the A.S.T.M. is continuing very active work on this subject, the trend in house paint evaluations is away from accelerated tests and toward actual house tests.

Group I, Subdivision VII, of Committee D-1 of the A.S.T.M. has been making a study to determine whether any known accelerated weathering test can be used to duplicate the fading results obtained on normal exterior south vertical exposure.

The initial study reported at the June, 1938, meeting covered:

(a) The accelerated exposure of a number of different tints made on one base.

(b) The results from a number of cooperators using the type of accelerated equipment available and the type of cycle standard with them at the time.

(c) The results from south vertical exposures by the same group of cooperators at nine different locations.

This first study showed fair agreement between the fading by exterior exposure at the nine locations and one particular accelerated test for fading. Furthermore, this one accelerated test closely approximated the average of the exterior south vertical exposures.

Additional tests reported at the March, 1942, meeting showed that:

(a) None of the accelerated weathering cycles tested can be used to predict fading performance of house paints with varying white base compositions.

(b) All the accelerated weathering cycles tested were too severe, and the rate of failure was so rapid that a distinction between the performance of individual paints was often not picked up between weekly examinations of the exposure panels.

### **Application**

**Wood surfaces** vary greatly in paintability or paint-retaining characteristics. According to Browne (12) the painting characteristics of a board depend primarily upon the amount and distribution of sum-

mer wood in it. Summer wood is the dense horny dark-colored portion of the annual-growth ring formed in the tree late in the growing season. It is made up of wood cells with very thick walls and small cavities and is in this sense much less porous than the spring wood, which is composed of cells with thin walls and correspondingly large cavities. Although liquids move more readily through the dense summer wood and paint oils are found to penetrate more deeply there, paint coatings do not seem to secure so firm an anchorage on summer wood as they do on spring wood. As a result, coatings exposed to normal conditions of weathering fail by flaking from the summer wood, leaving it bare, while the spring wood remains apparently well covered. All native soft woods contain both summer wood and spring wood; the proportions vary in different woods and in different boards of the same woods. There is, in fact, a greater variation in painting characteristics between spring wood and summer wood in a single board than there is between average boards of different woods.

The density, or weight per unit volume, of a soft wood board measures roughly its ability to hold paint coatings because boards are heavy or light according as they contain much or little summer wood. However, if a board has many annual-growth rings per inch it may have the summer wood confined to narrow bands and yet be moderately heavy. Such boards hold paint far better than boards of equal weight cut from more rapidly growing trees, in which the summer wood is present necessarily in wide bands.

In a test conducted by Forest Products Laboratory, the cedars, cypress, and redwood held paint best, and northern white pine, western white pine, and sugar pine did almost as well. With southern yellow pine and Douglas fir, which are abundantly available woods whose high strength makes them suitable for building construction, and with western larch, serious flaking of the coatings from the summer wood occurred sooner than with the other species tested. Western yellow pine, white fir, the hemlocks, and the spruces fell between the white pine group and the southern yellow pine-Douglas fir group.

It is of interest to note that Marshall, Iliff, and Young (48) rated the comparative paint performance of various types of lumber as follows: White pine was best, followed in turn by red cedar, western yellow pine, Douglas fir, Arkansas yellow pine, and long leaf southern pine. These results were obtained with unbacked panels. With backed panels red cedar was in certain instances rated better than white pine.

The wood of many species varies greatly in density and texture and therefore in painting characteristics. Thus, for example, light nar-

row-ringed boards of southern yellow pine or Douglas fir hold paint about as well as the wide-ringed boards of cypress, and light narrow-ringed boards of western yellow pine behave like white pines. Density and texture therefore afford a good basis for selecting the best wood to paint.

Knots and pitch play a large part in the grading of lumber. Since they give trouble in painting, the select grades of lumber, which permit few defects, are more satisfactory to paint than the common grades. Knots in the white and yellow pines seem to be more objectionable from the point of view of painting than knots in woods like the cedars, the hemlocks, white fir, and larch.

Edge-grained boards hold paint far better than flat-grained boards. This is because the bands of summer wood in the edge-grained boards are cut in such a manner that they are as narrow as possible. Among the flat-grained boards, those surfaced on the bark side (the side nearer the bark of the log) are more satisfactory to paint than those turned pith side out because there is less danger of the "grain shelling out." Some woods that hold paint best may give difficulty with grain shelling under these circumstances. Like selection by density and texture, selection by the kind of grain is difficult to apply to the purchase of many kinds of lumber because only lumber cut from very large trees can be economically segregated according to such classifications.

The A.S.T.M. specifications for western red cedar D358-38 (3), as recommended for accelerated weathering tests, state that the material shall be close-grained, as nearly edge-grained as possible, diverging not more than  $45^{\circ}$ . The wood shall weigh 22 to 23 pounds per cubic foot after at least one week's storage in a protected dry atmosphere. Similar A.S.T.M. specifications for white pine wood panels, as recommended for natural weathering tests, state that the number of annual rings per inch along the radius of the log shall be not less than 18. It may be flat or edge-grained as desired. Edge-grained wood is defined as that in which the grain intersects the testing surface at an angle of  $45^{\circ}$  or more. Flat-grained wood is defined as that in which the angle is  $15^{\circ}$  or less. The test surface of the flat-grained wood shall be on the bark side. The wood shall weigh 24 to 26 pounds per cubic foot, when in equilibrium with air at 60 to 65 per cent relative humidity and  $69$  to  $71^{\circ}$  F. It shall be free from knots, pitch pockets, pitch streaks, and other defects.

**Repainting**, as pointed out by Browne (12), should not be put off until the old coating has flaked badly and much bare wood is exposed.

The old coating serves as the foundation for the new one, and yet, if it is badly chipped and broken, the customary methods of repainting do not secure a first-class appearance and a durable repaint job. Very often coatings fail to give adequate protection against weathering long before they flake noticeably. This is especially true of flat-grained boards of some species that hold paint well because of their low content of summer wood. Conspicuous wood checks and cracks show clearly that the wood is no longer receiving sufficient protection even though the coating is apparently intact. Repainting neither heals nor conceals entirely weathering damage that has become conspicuous, but, if the wood is repainted promptly when minute wood checks begin to appear, it can be protected from weathering for a long time.

If the earlier paint is in a suitable condition the new paint can be applied directly after brushing away such loose chalk and dirt as may have accumulated. If, however, the earlier paint is not suitable for repainting because of bad paint failure, severe moisture conditions, or for other reasons susceptible of correction, the proper preliminary steps should be taken before proceeding with the repaint work. These include the removal of the old paint, elimination of leaks, and special treatment of sappy wood. The surface to be painted should be dry, and painting in damp or wet weather should be avoided.

The application methods most commonly used in applying exterior paints are brushing and spraying. Both application methods require considerable technique which can be developed by practice. Advice from experienced painters and from brush and spray gun manufacturers is often helpful and should be obtained if one is interested in doing such work. Vanderwalker (69) gives many details on this subject which should be useful to one seeking general information on house painting methods. Furthermore, several comparative tests of brush versus spray application of paint are discussed in considerable detail by Pickard (61).

**Reductions** of the paint to meet various conditions are usually given. Before any paint is applied it should be well stirred and thinned in accordance with the directions supplied with the paint. Such thinning practices are by no means uniform. As reported by Gardner (31), after making a survey of thinning directions, it is apparently impossible to prepare a set of standard reductions which would apply to all formulations of prepared paint. It is generally agreed, although there are exceptions, that the first coat should contain more oil and be somewhat thinner than the second coat, which in turn should contain more oil and be somewhat thinner than the top coat. Ordinarily

the more absorptive the surface the greater the amount of oil used in the reduction. It is common too to use more thinners in cold weather than in warm weather to maintain good application properties. In two-coat repaint work the usual practice is to use the first coat and the top coat reduction procedures.

**Aluminum priming** is commonly recommended on all kinds of new lumber (1). Generally, it is recommended for those woods that present some paint-holding difficulties, such as yellow pine, Douglas fir, ponderosa pine, spruce, and hemlock. It is also recommended for coating:

(a) Wood which has begun to weather, showing cracks and checks and a roughening of the surface fibers.

(b) Creosote-stained shingles where light-colored top coats are desired. The leafed flakes of the aluminum pigment serve to prevent the stain from "bleeding" into the top coats and discoloring them.

(c) Knots in lumber, as these are often a cause of early paint failure or discoloration of the finish coats. It is recommended too, however, that the aluminum paint when dry should be covered with a good-quality white shellac before the top coats are put on. Actually, shellac is commonly used without the aluminum paint. From the standpoint of preventing staining it is very effective. Shellac, if used excessively, however, may cause flaking trouble. Neither method is entirely satisfactory.

Aluminum priming is not recommended as a cure-all for moisture failure. Furthermore, when the paint on a building to be repainted is still sound and no checking of the wood has occurred, it is considered unnecessary to use an aluminum first coater.

Exposure results indicate that the more adverse the wood condition and the poorer the quality of the house paint used, the greater the advantage for the aluminum primer in comparison with three-coat self-primed systems. This means of course that the better the house paint used and the better the condition of the wood to be painted, the less the advantage, if any, for the special aluminum primer.

As pointed out by Browne (15), aluminum priming has the disadvantage of requiring two coats of white or of light-colored finishing paint to hide its color adequately.

According to Wray (71), the excellent performance of aluminum primer can, in part, be ascribed to its high moisture impermeability and excellent adherence to both spring and summer wood. By reducing

rapid changes in the moisture content of the wood, swelling and shrinking are kept at a minimum.

**Two-coat systems** on new wood have been promoted quite generally in recent years by various paint manufacturers with considerable success. Such systems are based primarily on non-penetrating type primers. According to Robertson and Hoback (63) the use of one coat of a properly formulated non-penetrating primer with high pigmentation is equal to two coats of ordinary penetrating types, as now reduced and applied. This is stated to be an important economic factor.

It is generally recognized, however, that two-coat systems on new wood do not show durability characteristics comparable to good three-coat systems. Two-coat systems on a south vertical exposure tend to show early erosion failure.

Actually the two for one claim for non-penetrating primers is hardly supported by the following film thickness data as obtained from two commercial three-coat system and two commercial two-coat system house paints. Data on these paints are:

Paint No.	Commercial Three-Coat Systems Applied as Two-Coat Systems		Commercial Two-Coat Systems	
	1	2	3	4
First coat reduction per gal.	1 pint linseed oil	1 pint linseed oil	½ pint turpentine	none
Gal. wt.	13.51	13.24	14.92	20.35
Consistency	82	82	65	84
% volatile by vol.	11.8	11.0	20.5	16.1
Approx. pigment volume in %	25	25.2	40	34
Top coat reduction per gal.	none	none	½ pint linseed oil	none
Gal. wt.	14.15	13.80	15.14	19.80
Consistency	90	90	72	90
% volatile by vol.	13.3	12.7	3.5	13.2
Approx. pigment volume in %	28.6	28.5	28	28.7

These commercial paints were applied over edge-grained white pine at 450 square feet per gallon for the first coat and 550 square feet per gallon for the top coat.

	Commercial Three-Coat Systems Applied as Two-Coat Systems		Commercial Two-Coat Systems	
Paint No.	1	2	3	4
First coat thickness, inches				
Theoretical	0.00353	0.00325	0.00280	0.00297
Actual	0.00211	0.00227	0.00219	0.00227
Penetration	0.00142	0.00098	0.00061	0.00070
First and top coat thickness, inches				
Theoretical	0.00605	0.00583	0.00542	0.00545
Actual	0.00442	0.00451	0.00427	0.00428
Penetration	0.00163	0.00132	0.00115	0.00117

In obtaining the above figures the amount of paint applied to each panel was determined by weighing the brush and container before and after each application. The areas painted were recorded and, from these data, theoretical film thicknesses were calculated.

The actual thickness of the dried films on various specimens cut from the panels was measured by means of a microscope equipped with a calibrated ocular. Several specimens were required from each panel and several readings were taken on each specimen in order to arrive at reasonably accurate film thickness values.

The difference between the theoretical film thickness and the actual film thickness was considered as measuring penetration.

As may be seen from these data, the commercial three-coat systems when applied as two-coat systems gave film thicknesses essentially equal to those obtained from the commercial two-coat systems.

It is true that there are indications of slightly greater penetration for the commercial three-coat system paints; however, the greater solids content in these paints is a compensating factor and the actual film thicknesses are comparable.

According to Browne (13), durability is a function of film thickness. Good performance is claimed for two-coat painting with a special primer and finish paint as made for application in thick coats. Basing his claims on a statistical study of thousands of houses, Long (46)

says that properly prepared and applied two-coat systems have superior durability.

### Paint Failures

**Can stability** is a requirement which must be met by a good exterior paint. Paints which are generally most stable are made with a linseed oil of relatively low acid number and with relatively non-reactive pigments. It is true that acid refined linseed oil is used in large amounts for outside house paints. It is also true that acid refined linseed oil gives better wetting and grinding characteristics than alkali refined linseed oil. Nevertheless, the acid number of the linseed oil used should be held fairly low and constant, especially if reactive pigments are present, in order to prevent excessive soap formation as well as excessive consistency variations on aging.

Granulation is the result of the deposition throughout the paint of small masses of metallic soaps of limited solubility by virtue of the inability of the oil to carry in solution all the soaps formed. Holley (37) points out that zinc soaps are the usual offenders and discusses many factors which enter into this unfinished paint problem. One of the most active factors in developing granulation is elevated temperature. Other contributing factors are the presence of air and moisture. The character and quantity of drier used also have an influence. Rosin driers, for example, are strong inciters to granulation, whereas linoleate driers high in lead and low in manganese are among those which are less detrimental.

Suspension is another factor in can stability which must be controlled. It is generally known and recognized that the use of high bulking pigments is helpful in connection with this control. Pigments and extenders of high specific gravity are prone to settle out of most paint vehicles. Extenders other than magnesium silicate, such as silica and barytes, will bear careful watching from the standpoint of suspension. Magnesium silicate, however, is known to be useful in outside house paints in connection with the prevention of hard caking. The wetting characteristics of the oils used also deserve consideration. In this connection Q (4.35 poises) bodied linseed oils are known to give excellent suspension and wetting characteristics, whereas Z (22.7 poises) bodied linseed oils give poorer suspension and poorer wetting (55). Good wetting driers which tend to give a flocculated pigment condition rather than a well-dispersed pigment condition are also helpful in obtaining improved suspension properties.



After-thinning is sometimes encountered, especially with highly false bodied house paints. This is particularly true when such paints contain limited amounts of water. The condition in most cases is caused by progressive wetting of the pigment by the vehicle. Any steps which can be taken to obtain a thorough wetting of the pigment by the vehicle, such as including the Q bodied linseed oil in the mix or sweating the paste overnight before reducing, are usually helpful in controlling this condition.

After-thickening, on the other hand, may result if the paints are made with vehicles of a relatively high acid number, especially if the paint contains reactive pigments.

**Film stability** is of course an essential feature of a good house paint. As pointed out by Broeker (9), a house paint, to give complete satisfaction, must be designed to have three characteristics all equally important.

- (1) It must retain a good appearance throughout its life.
- (2) It must provide adequate protection to the surface for a sufficient period of time.
- (3) It must yield a film satisfactory for repainting without the necessity of burning, with the consequent additional expense.

For a paint to retain a good appearance throughout its life, it must show good resistance to dirt collection, to discoloration from screens, metal fixtures, etc., and to mildew growth. In the class of tinted house paints it is also necessary that the paint show good resistance to fading. The film should begin to chalk within a reasonable time to clean away any slight dirt and metal discoloration which may collect on the surface, and the chalking effect should be uniform so that the film does not take on a splotchy, uneven appearance either with respect to cleanness or color.

The paint must have excellent resistance to checking, cracking, and flaking type failure. Once the film integrity is destroyed by cracking type failure, the paint no longer provides protection to the surface on which it is applied. If the film failure progresses to flaking or loss of adhesion, the surface is no longer satisfactory for repainting without special preparation such as scraping or burning.

It has been necessary, therefore, to design house paints which will fail primarily by chalking. This chalking rate should not be too rapid. The film should not become thin in less than four to five years, if the home owner is to receive a fair value for the money expended.

Definitions and illustrations of the various types of film failures have been established by the New York (54) and the Philadelphia (60) Production Clubs. The more common exterior paint failures are described as follows:

**Discoloration** is an alteration in the original color of a film. Every alteration in the original color is implied, e.g., yellowing, darkening, fading, mottling, bronzing, dirt collections, and mold growth. Figure 6 shows discoloration caused by copper staining.

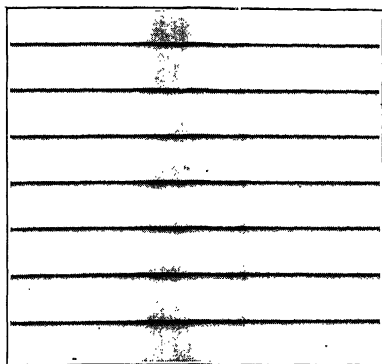


Fig. 6. Discoloration from Copper Staining.

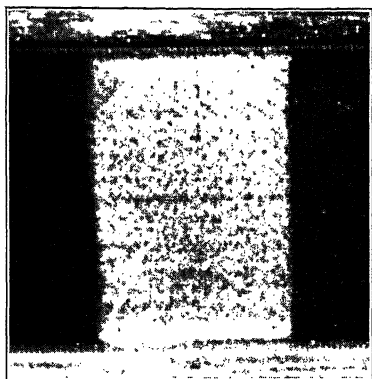


Fig. 7. Black Velvet Chalking Test.

**Chalking** is a phenomenon of coatings manifest by the presence of a loose powder, evolved from the film itself at or just beneath the surface. Chalking may be detected by rubbing the film with the fingertip, or preferably with a piece of velvet of contrasting color. Figure 7 shows a black velvet chalking test.

**Checking** is that phenomenon manifest in coatings by slight breaks in the surface of the paint film. The break should be called a check if underlying paint coats are visible. Where precision is necessary in evaluating a paint film, checking may be described both as "visible checking" (as seen with the naked eye) and as microscopic checking (as observed with a 10-power magnification as recommended by the A.S.T.M.). The use of a microscope to detect and evaluate incipient checking is recommended. Figure 8 shows characteristic checking failure.

**Cracking** is that phenomenon manifest in coatings by a break extending through to the base surface. Where it is difficult to determine whether this is the case, the break should be called a crack if the

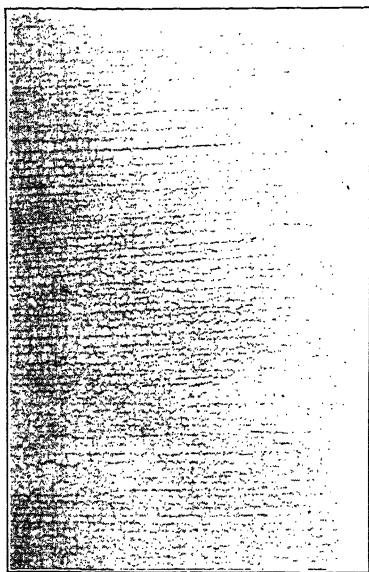


FIG. 8. Checking.

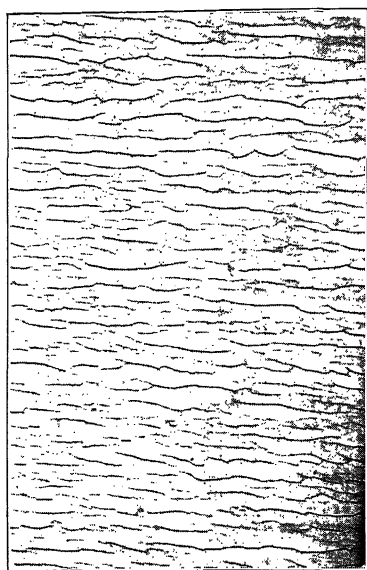


FIG. 9. Cracking.

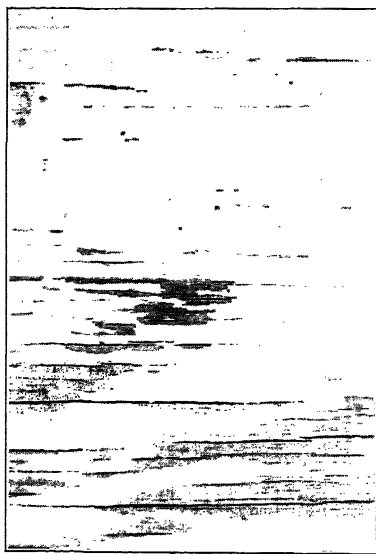


FIG. 10. Flaking.

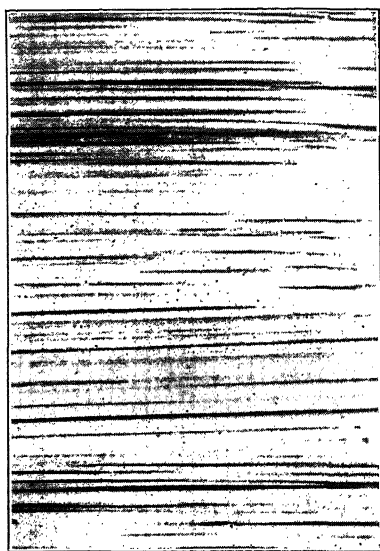


FIG. 11. Erosion.

underlying surface is visible. Figure 9 shows characteristic cracking failure.

**Flaking** is a phenomenon of coatings manifest by the actual detachment of pieces of the film from its substrate. Figure 10 shows characteristic flaking failure.

**Erosion** is that phenomenon manifest in coatings by the wearing away of the finish to expose the substrate. It occurs as a result of chalking. The degree of failure is dependent on the amount of substrate visible. Figure 11 shows characteristic erosion failure.

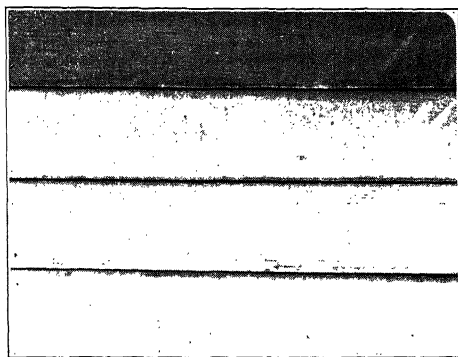


FIG. 12. General Appearance.

**General appearance** is the complete impression conveyed when the panel is viewed at a distance of ten feet before any detailed inspection has been made. Figure 12 shows the general appearance of four paint panels where the differences observed are due to variations in dirt collection and self-cleaning characteristics.

**Mildew collection** is defined as the phenomenon of a coating manifest by the presence of mold or fungus growth of a type familiarly known as mildew. Two types are common: (1) the spore type which resembles caviar in appearance and (2) the mycelium or filament type. A microscope is often necessary to differentiate mildew from dirt collection. Figure 13 shows characteristic mildew collection.

**Mildew prevention** has received considerable attention in the study of exterior paints (6). An excellent review of the work done was prepared by the Dallas, Fort Worth Paint and Varnish Production Club (19). Also, extensive tests have been made and reported by Gardner (28) and his co-workers.

It is generally agreed that zinc oxide is the only common pigment which is greatly toxic to mildew, and for this reason it is a most valu-

able aid in minimizing and controlling such fungus growths. The effect of zinc oxide is directly proportional to its concentration in the film.

Of the many chemicals which have been tested as fungicides in exterior paints, the mercurials have invariably proved their superiority. For effective results bichloride of mercury may be added to the paint to be used for finishing coats in quantities of about one part in 500 to 900 parts of paint according to the prevailing severity of the mildew growth.

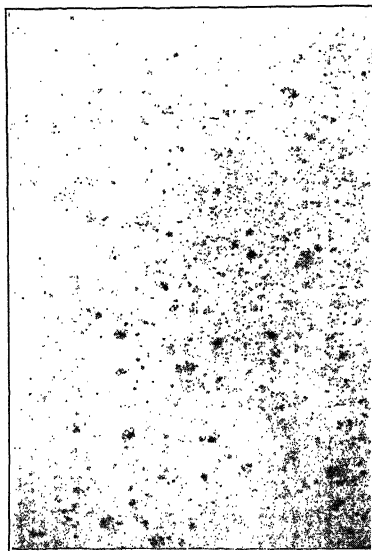


FIG. 13. Mildew.

Red cuprous oxide, 5 per cent or more, may be used with very effective results in colored paints.

Other chemicals much safer to use but not giving as good results are thymol, sodium silico-fluoride, phthalic anhydride, Dowicides, and Monsans.

To secure favorable results, all badly mildewed exterior surfaces should be washed prior to repainting. An effective solution for this purpose may be made by dissolving one pound of trisodium phosphate in one gallon of water. After scrubbing, the surface should be flushed with clean water. Very bad cases may be treated with one part of bichloride of mercury to 300 parts

of water. (Precaution should be taken to prevent this solution from coming in contact with the skin.) After the surface is dried the finishing coats of house paint may be applied.

**Moisture failure** of exterior paints is a problem which is becoming increasingly important in certain sections of the country. A considerable amount of work and study has been applied to this problem and much has been learned concerning the causes and the mechanism of this failure. Browne (14), Hartwig (34), Teesdale (65), Gardner (30), and Iliff and Davis (40) have all published excellent papers on the subject.

It is generally agreed that constructional defects as well as humidification and insulation without sufficient ventilation or supplementary means of protecting exterior walls from moisture are extremely important factors in causing paint failures.

The more important moisture sources are considered to be condensation and direct water contact. A temperature gradient through the wall with paint on the cold side is necessary for failure resulting from condensation. A temperature gradient through the wall with paint on the cold side accelerates failure by direct water contact. Moisture failure rarely occurs until the wood at the paint wood interface approaches or reaches saturation. Moisture failure does not occur with a film whose integrity is low enough so that moisture will pass out as rapidly as it appears. None of the common types of paint have sufficient permeability to prevent failure. New and flexible paint films fail by blistering and, as the rigidity of the film increases, blistering becomes peeling. For this reason repaint jobs over old paint usually show only peeling failure.

Tar paper is rated as having only a limited favorable effect in the prevention of moisture failure. The blocking of air circulation behind the painted areas has an adverse effect. Within certain limitations the sealing of the interior moisture from the exterior painted surface has a favorable effect and the introduction of exterior air behind the painted areas has a very favorable effect.

Much additional work is needed on this problem in order to point the way to decreased paint failures as encountered under adverse conditions. Study should be made of the effect of variations in such properties as permeability, adhesion, penetration, film toughness, etc., as related to moisture failure.

**Factors related to film failure** and the importance of each are not too well understood. According to Hunt and Lansing (39), outdoor exposure factors which contribute to the failure of protective films are ultraviolet light, oxidation, temperature, and humidity. It is known that both heat and moisture have a plasticizing action and that a certain degree of plasticity is desirable in protective films. Experiments on films of oil type compositions show that both ultraviolet light and oxidation play important roles in the aging phenomenon, and it is not unlikely that the deteriorating effect of ultraviolet light is associated with its catalytic effect in promoting oxidation.

MacGregor (47) takes a somewhat different view. In discussing the difference in the rate of perishing on north and south exposures ultraviolet light is rated as a factor. However, it is stated that the difference in the selective absorption of these rays is not a measure of the rate of perishing and it does not change the character of the perishing. It seems that the effect of the action of ultraviolet has been overemphasized. The difference in performance of paints on

these two exposures is in degree or magnitude, not in type. A definite difference between the conditions of these exposures is heat. A moisture-laden film is swollen. When exposed to direct sunlight it will quickly become dry on the surface, but it will lose the moisture in the underlying portion of the film at a much slower rate. This will set up a stress in addition to that normally encountered in oil gels and will cause rapid disintegration. The north or shaded surface will not surface-dry, but will dry slowly throughout and thus no additional stress will be imparted to the film.

Blom and Krumbhaar (8) have prepared interesting photographs which show the colloidal state of film-forming materials, film effects produced by ultraviolet light and various driers, and the formation of various soaps. The pictures and discussion are helpful and instructive. It is shown clearly that a film breaks at its weakest spot as soon as the internal stress exceeds its tensile strength at the same weak point and it demonstrates spectacularly the play of elastic forces around the points of breaking. Durability advantages are indicated for lead and manganese over cobalt as drier and for lead over zinc soaps and for smooth over irregular surfaces.

A considerable amount of work is being done on temperature and humidity effects on paint films as indicated by recent preliminary papers on this subject (18, 33). However, the mechanism of exterior paint failures is complicated and much additional information is needed on the pertinent variables involved.

### Special Paints

**Trim paints** are used extensively in present-day outside house paint practice. Reddy (62) states that in such paints there appears to be a definite trend away from linseed oil toward 100 per cent synthetic vehicles. The proportions of linseed oil to fortifying resin vehicle are not fixed, however, as the resin varnish content may vary from 25 to 100 per cent, depending on the viewpoint of the formulator. The consistencies of vehicles will naturally vary and the incorporation of extender becomes a function of the viscosity desired.

In order to insure color permanency many formulators, averse to any extender, practically eliminate linseed oil, even at a noticeable sacrifice in brushing characteristics. Others feel that a compromise is necessary and incorporate both extender and oil.

The accepted practice in setting up a trim paint is first to determine the oil resin ratio that is to be used and then to work out a

pigment to binder ratio which will yield satisfactory hiding and performance.

Another practice which is followed to some extent is to incorporate a small complement of varnish, 10 to 15 per cent, as a reinforcement for regular house paint vehicles. In many instances this fortification finds application in the darker house paint shades normally used for trim.

Parker and Cronin (59) report from trade contacts that long oil alkyd resins, either linseed or soybean type, are most commonly used for fortification.

According to a survey conducted by Parker and Cronin, green is the preferred trim color. The actual analysis given for this survey is found in Chapter 10B, page 315.

**Porch paints** were often prepared in the very early days by adding a spar varnish to a house paint and tinting to the color desired. This procedure gave fair results, depending on the combinations used. Such paints often showed objectionable after-thickening due to reactions between the varnish acids and the active pigments present in the house paints. The tendency too was toward cracking and flaking type failures probably caused by excessive hardening of the films coupled with insufficient flexibility and toughness.

In more recent times various varnish vehicles have been used. Obviously, for best results these vehicles should be carefully selected for hardness and toughness as well as for resistance to light, air, and water. Since porch paints are very competitive, it is often true that price is the controlling factor in the selection rather than quality. Practically all the larger vehicle manufacturers offer varnishes especially designed for porch or deck paints or enamels, and such sources should be consulted for further vehicle information.

The pigments used should be of the chalk and fade-resistant type since gloss retention and fade resistance are important. The pigmentation may be of a paint or enamel variety. Porch paints generally carry somewhat higher pigment volumes and more extender than the enamels. In any event, special care should be taken to make sure that the pigments and vehicle used are compatible. Such paints or enamels should be carefully checked for can stability, application properties, and durability.

**Stucco, brick, and artificial shingle paints** are receiving more and more attention. Generally, paints which are designed for any one of these surfaces can be successfully used on the others. Gardner (29),



Parker (57), and Sentel (64) have recently published interesting articles on such finishes.

It is generally agreed that the greatest danger in painting such surfaces, particularly if they are relatively fresh, is free alkali. When free alkali is known to be present it is customary to wash the surface with a solution of about two pounds of zinc sulfate in a gallon of water. This helps to neutralize the alkalinity.

When painting such surfaces it is common practice to apply a primer prepared by fortifying the first coat outside house paint to be used with an equal volume of a good spar varnish. This is followed by two coats of regular house paint. On weathered surfaces, where the alkalinity, is not high, somewhat better results are usually obtained by using regular house paint without the varnish fortification in the first coat. In certain instances where penetration is excessive it is desirable to coat the surface with boiled oil before applying the house paint.

In the formulation of special paints for masonry walls there appears to be a trend toward the use of high pigment volumes and selected oils with and without varnish fortification.

Chlorinated rubber paints are used to some extent on raw masonry. They are considered to be quite useful on such surfaces owing to the fact that this type of vehicle is relatively inert to the alkali present in the substratum. Chlorinated rubber paints are hard to apply on account of the fast evaporation of the special solvents required. As development goes on, these paints probably will be improved in this respect; however, such paints are still largely in the experimental stage and the extent of their use remains to be seen.

Other paints which are receiving serious consideration for masonry structures include cement-water paints, emulsified synthetic resin paints, synthetic rubber coatings, emulsified rubber paints, and various specialized coatings.

**Paints for metal surfaces** are often required in connection with exterior finishes for houses. The metals to be painted may be of the ferrous or non-ferrous type. In finishing many such metals a special pretreatment and in certain cases the use of a special primer are the normal accepted practice.

A great deal of information is available on metal protective paints. In this connection Nelson (50), Dorsey (21), Van Sieten (70), and Parker (57) have published interesting papers which deal with various phases of finishes for various metals. Burns and Schuh (16) have

written an excellent discussion which covers the use of paints for the protection of metals against corrosion.

Galvanized iron is one of the most troublesome metal surfaces to paint because of the adhesion difficulties which are so often encountered when organic finishes are used over zinc. Pretreatment recommendations have included light sand blasting, special washes of the phosphate and chromate type, and exposure for a period of at least six months before painting. These precautions are helpful but not very satisfactory, especially under somewhat less readily controlled conditions. In recent years, however, special galvanized iron primers have been developed which have excellent adhesion. Most of these new type primers are based on the use of zinc dust which is mixed with the vehicle just before using. Such zinc powder paints as used with various vehicles are reported as giving excellent service (5).

In painting iron or steel it is agreed generally that the surface must be scrupulously cleaned to remove all mill scale, rust, grease, etc. Sand blasting is regularly accepted as the best method of cleaning. Wire brushing or sanding can be considered as fairly effective. When the surface is clean, it should be primed immediately to prevent further rusting. Special primers are generally used for this purpose. They are formulated to retard corrosion and to carry such pigments as zinc yellow, basic lead chromate, and red lead. Basic pigments that are good neutralizing agents are normally considered helpful.

The vehicle used should have good wetting and adhesion properties. It is now rather generally recognized that resins with polar OH and COOH groups are desirable for improving the adherence of primers. In so far as possible it is desirable to use systems which are high in resistance to water or moisture.

It is the prevailing practice to cover the primer with one or two coats of trim paint. Aluminum paints and regular house paints are also used to a considerable extent over such metal primers.

Practices similar to those previously described are also used in the painting of bronze or copper. In fact zinc dust paints are especially recommended for screens as such paints not only protect the screens from corrosion but also prevent the formation of discolored areas so often observed under screened windows (53). The only pretreatments suggested as desirable are washing with toluol, light gasoline, or a suitable solvent to remove the light coating of grease normally found on such material. A brief weathering period of one to three months will usually clean and etch such surfaces sufficiently.

Trim paints of the fortified type, thinned as required with turpentine, are also used with reasonable success on screens to prevent corrosion and staining.

In painting aluminum, adherence is a very definite problem. Aluminum alloys differ somewhat in adherence properties, and those which contain magnesium generally give less favorable results (22). Oxide films on aluminum are helpful in giving improved paint-holding properties, and chromate solutions have a powerful effect in repairing and maintaining the integrity of the oxide film upon aluminum without increasing appreciably the film thickness. Zinc yellow is known to give excellent performance when used in priming coats on aluminum (58). Trim paint, aluminum paint, or regular outside house paint can be used over the primer for such additional protection as may be required.

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## CHAPTER 10B

### EXTERIOR TRIM PAINTS

DEAN H. PARKER

A class of house paints which might warrant a somewhat more extensive discussion than has already been devoted to them in this book are the greens, blues, blacks, browns, and other comparatively dark colors which are used principally on the trim, screens, shutters, and other small areas of buildings. Paints in these colors are generally known as trim paints since they are usually formulated especially for application to these surfaces.

Some idea of the relative importance in volume of sales of the various trim colors may be obtained from the following table which shows the results of a survey of over 3,000 houses in the better-class New York suburban areas to determine the actual color distribution as it exists at present. Only those houses were included in the survey which had trim decoration in the darker colors, the others being disregarded.

COLOR	HOUSES	PER CENT
Dark green .....	963	29.0
Med. green .....	535	16.0
Lt. green .....	430	12.9
Black .....	405	12.1
Brown .....	328	9.7
Dark blue .....	147	4.4
Med. blue .....	137	4.1
Lt. blue .....	64	1.9
Maroon .....	233	7.0
Red .....	65	1.9
Orange .....	20	0.6
Yellow .....	13	0.4
Totals .....	3,340	100.0

It will be seen that the greens account for well over half of the total, as might be expected. Green was used on 57.9 per cent of all houses painted with trim colors.

Black is rapidly gaining in popularity in the newer housing developments. White houses with black shutters make an excellent contrasting combination.

Brown trim is used to a large extent on houses built in the English style of architecture. A great many of these are to be seen in developments constructed in the period from 1920 to 1930.

Blue is rapidly becoming one of the most popular trim colors. It is observed a great deal on shutters of dwellings recently constructed and already amounts to over 10 per cent of the total, with a tendency toward still greater popularity.

There is also a noticeable trend toward the use of maroon and dark red shutters in new residential developments. Very attractive effects are produced by painting dwellings white or cream and setting off this color by red composition-shingle roofs and maroon or red shutters.

Orange and yellow have not been employed to any great extent up to the present time, although a number of houses on which they were used were observed in districts built up within the last couple of years.

There is also considerable demand for the brighter red, blue, orange, and yellow trim paints for uses other than dwellings, such as store fronts and service stations.

The following twelve colors are suggested as the basis for a comprehensive line of trim paints, although a smaller or larger number could be used at the option of the paint manufacturer, depending upon the requirements of his trade.

Dark green	Maroon
Medium green	Dark blue
Light green	Medium blue
Jade green	Light blue
Black	Bright red
Brown	Yellow

The particular shade of each of these colors to be included in the line should be properly chosen, taking into account consumer appeal as well as the practical aspects of pigment availability, cost, durability, and other physical properties.

The greens and blues should be selected to give distinct differences in depth of shade. Many paint manufacturers make the mistake of not having enough contrast between the various shades shown on their color cards.

The bright red and yellow might not be sold in very large volume but their inclusion provides for a range of color instead of single shades. For instance, by blending the bright red with the maroon in varying proportions a range of dark reds could be produced. Similarly, the bright red could be blended with the yellow to give orange if such a color is desired.

It will be noted that a bronze green has not been included although many manufacturers sell such a product in their trim-paint line. Bronze green shades may be easily made from the dark or medium green by mixing with yellow and black. The medium green might be omitted since it may be made by blending the light and the dark. It is included, however, since most paint men will agree that it is the largest selling color of the entire group.

# PROPERTIES OF TRIM PAINTS

The properties which must be considered in the formulation of trim paints are:

Color	Drying
Consistency	Initial gloss
Brushability	Gloss retention
Leveling	Color retention
Running	Durability
Hiding	Package stability
Flooding	

## Color

The color of the trim paint obviously will depend upon the pigments used to make it. These pigments should be selected, however, taking into account their effect on all the other properties listed above, in addition to the color. Attention should also be given to the behavior of the pigments when the various trim-paint colors are blended with each other. This is a very important point since many pigments are fairly durable when used alone in a protective coating but fade out very rapidly when blended with other colors.

## Consistency

Satisfactory consistency or "body" may be produced in paints and enamels by (a) the pigment, (b) the vehicle, (c) various bodying agents, or by combinations of the three methods.



Linseed oil house paints made with vehicles consisting largely of raw linseed oil are typical of products bodied principally by the pigment. Such paints must be heavily pigmented with prime pigment and extender to give them proper consistency, since the vehicle itself has a very low viscosity.

High-gloss enamels are representative of coatings obtaining their body principally from the vehicle. They contain a relatively small amount of pigment compared with house paints but are made with varnish vehicles of much higher viscosity than raw linseed oil.

Bodifying agents such as water emulsions, heavily limed oils, and zinc stearate are seldom depended upon by themselves but are ordinarily used in conjunction with the other two methods for increasing the viscosity of paint products.

Trim paints are made in both types of products mentioned above as well as combinations of the two in all proportions. Such blends would of course depend for their body partly on the pigment and partly on the vehicle, and may or may not contain accessory bodying agents.

Many trim paints are inclined to be somewhat "puffy" and possess a considerable degree of thixotropic body. Viscosimeters of the paddle type such as the Krebs-Stormer are therefore somewhat more suitable for control instruments than some others such as the orifice type viscosimeters.

The average consistency of trim paints as manufactured is somewhat lower than that of the lighter-colored house paints. The latter are generally packaged at about 80 to 100 KU (Krebs Units) on the Krebs-Stormer Viscosimeter whereas the trim paints are usually packaged at about 70 to 80 KU.

### Brushability

Good brushability is an important property in trim paints as affecting sales resistance on the part of the consumer. It is very important that the products be so formulated as to be applied with a minimum of effort.

At present there is no entirely satisfactory method of quantitatively determining the brushability of trim paints. The measurement of this property is largely a matter of personal opinion arrived at by brushing out the paint on a large enough surface to be able to estimate the drag under the brush.

Trim paints made with raw linseed oil as the vehicle generally have excellent brushing characteristics owing to the high degree of

"slip" possessed by the oil. When varnishes or bodied oils are introduced into the formulations, brushability tends to become poorer as the raw linseed oil content is decreased, and may develop into a serious problem in products containing little or no raw oil.

Brushability may, of course, be improved by formulating with a higher raw oil content. The use of solvents having slow evaporation rates is helpful. Increasing the pigment and volatile at the expense of the binder in a formulation high in varnish tends to improve brushability although the procedure may be impractical in many products on account of cost, if the pigmentation is expensive. There is also a limit to the level to which the pigment-binder ratio may be raised without lowering the gloss.

### Leveling

Good leveling or freedom from brush marks is a fairly important property in trim paints. In general, the leveling is roughly inversely proportional to the amount of raw linseed oil in the vehicle or, in other words, paints high in raw linseed oil tend to show poorer leveling than those made with a large proportion of varnish in the vehicle.

Some pigments, particularly those which impart a puffy, thixotropic nature to the paint also interfere with the leveling of trim paints.

### Running

Running is the tendency of a paint to sag and curtain when applied to vertical surfaces. It is closely related to yield value. Running often accentuates flooding, particularly in paints made from chrome greens, as will be discussed later. A high resistance to running is obviously very necessary for properly formulated trim paints, since they are so often used on sash or adjacent to paints of other colors. Paints of poor running resistance tend to run down onto adjacent paint surfaces, giving an appearance of careless workmanship, whereas the painter might have applied the paint with exemplary technique.

The running tendencies of trim paints may be determined by applying them to non-absorbent vertical surfaces at a normal spreading rate of about 500 square feet per gallon and allowing them to dry. Many proprietary trim paints fail in this test, running down over the smooth non-absorbent surface as they would over the glass of a window when used to paint the sash. The test is, of course, only a rough one, but has considerable value in the hands of an experienced oper-

ator. It requires careful technique, particularly, in the application of the paint in a uniform film along the bottom edge of the painted area.

Running may sometimes be overcome by the use of additive agents which function in various ways, such as causing bodying or partial flocculation. Two per cent of water emulsion is often effective in decreasing running. Elimination of running is best accomplished, however, by reformulation of the paint, increasing the consistency with bodied oil, varnish, or pigment.

The pigment affects running in varying degree, depending upon the type of vehicle used. The pigment type, particle size, paint thickening power, dispersion, and concentration are all factors influencing the performance of the paint. Paints which are unsatisfactory in resistance to running may often be improved most easily and satisfactorily without increase in formulation cost simply by the use of a pigment of higher oil absorption if obtainable in the same depth of shade.

### Hiding

A simple method of determining hiding power is by making paint-outs over backgrounds comprising both black and white areas. Hiding power may be expressed in terms of coverage in square feet per gallon to make these areas practically indistinguishable from each other. Lacquered sheets made from heavy paper containing an area of one square foot, with a border for convenient marking and handling, are quite satisfactory for the purpose.

The technique used for determining hiding power is fairly simple and yields results which are probably accurate enough for all practical purposes. The paint is merely brushed out evenly on the sheet to practically complete hiding and the weight of paint determined by weighing the sheet before and after application. If the weight per gallon of the paint is known, the spreading rate in square feet per gallon may easily be computed.

If it is desired to apply paint at a certain spreading rate, a glass syringe graduated in cubic centimeters may be used to measure the

CC. PER SQUARE FT.	SQUARE FT. PER GALLON	CC. PER SQUARE FT.	SQUARE FT. PER GALLON
3	1,260	10	378
4	946	11	344
5	757	12	315
6	632	13	291
7	541	14	270
8	473	15	257
9	420	16	236

desired volume. The volume of paint which must be applied to an area of one square foot to give various spreading rates may be read from the table on page 320.

### **Flooding**

Flooding is, of course, the tendency of certain paints, particularly those made with chrome greens, to develop streakiness or uneven color owing to pigment particle migration (2). Any flooding is generally accentuated in paints having a tendency to run but it almost never develops in products of high running resistance. Formulation changes to reduce running will often tend to decrease flooding. Bodying up the paint is a good method of reducing flooding. There are also many agents, and special treatments which under certain conditions and in specific paint systems will have a tendency to reduce flooding, although none of the agents or treatments are positive in their effect in all systems. Some will actually decrease flooding in one system while increasing it in another. Soya lecithin and Wecoline oil have proved effective for decreasing flooding in certain instances.

### **Drying**

The rapid drying of a paint to a tack-free surface has always been an asset in its general property scheme. The chief advantage of this lies in the fact that dirt collection is cut to a minimum and thereby the color is protected to a definite degree. Rapidity of drying is also desirable to carry the freshly applied paint quickly past the danger of damage from suddenly arising rain storms which might cause water spotting. Drying, as is well known, is usually a function of the vehicle system. Only to a small degree does it depend upon the pigment. In general, the drying time of trim paints is shortened as raw linseed oil is replaced by varnish.

### **Initial gloss**

No particular comment need be made on this property except to point out that rough spots, cracks, and other irregularities in the substratum are often more apparent on close inspection when a high gloss paint is applied over them than when a paint of somewhat lower gloss is used. When viewed from the distance at which most house paint jobs are observed, it is rather difficult to detect quite wide differences in the gloss of trim paints. It would seem, therefore, that it is not particularly important and may be actually undesirable under some

conditions of application for trim paints to have a high gloss such as the public has come to expect in automobile finishes.

It is, of course, axiomatic with paint technicians that gloss is influenced by practically all the elements of a paint formula, including the pigment, the vehicle, and the pigment-vehicle ratio. In general, the gloss of trim paints is made higher by replacing raw linseed oil with varnish, by reducing the extender content, and by lowering the pigment-binder ratio.

### **Gloss retention**

Good gloss retention in a trim paint subjected to exterior weathering is desirable but not absolutely essential. As long as the shutters or other surfaces on which the paint is applied retain their original color or even maintain a reasonably attractive color, although showing a definite change from the original shade, the consumer is usually satisfied. As has been mentioned before, the gloss, if any, of a painted surface is difficult to observe by casual inspection. It is necessary to observe the surface from the correct position with regard to the angle of incidence of the sun's rays in order to determine whether any gloss at all is apparent.

### **Color Retention**

Color retention is probably one of the most important properties to be considered when formulating a line of trim paints since they are primarily decorative and secondarily protective. The major portion of the formulator's efforts should be directed toward the production of goods of as high color-retentive properties as possible, provided the other properties of the product are not outstandingly inferior.

In addition to actual resistance to fading or darkening, mildewing and dirt collection are closely associated with the color-retentive properties of a paint since they both affect its appearance. Streakiness or uneven color is also undesirable. A product which fades more rapidly but uniformly is to be preferred over one which becomes streaky or blotchy.

### **Durability**

The resistance to checking, cracking, peeling, scaling, flaking, and other forms of film failure of trim paints must also be reasonably good or premature failures will occur which are likely to leave the substratum in poor condition for repainting and may involve expensive surface-cleaning operations. It is necessary, therefore, in considering

new types of vehicles or pigments for use in trim paints to evaluate them thoroughly under conditions as close as possible to those to which the paint will be subjected in actual use.

### Package Stability

No particular comment is necessary on the property of package stability except to point out that trim paints, like any other line of shelf goods, must be formulated carefully for keeping qualities and easy re-mixing in preparation for use. The paints should not show excessive increase or decrease in consistency and should dry satisfactorily for a considerable period of time after manufacture, since they may possibly remain in stock for several years before being sold.

### VEHICLES USED IN TRIM PAINTS

The use of varnish in vehicles for trim paints is probably much more common practice than in vehicles for ordinary house paints for a number of reasons.

White and light-colored house paints are made at present for the most part with vehicles consisting largely of raw linseed oil with a comparatively small proportion of bodied oil sometimes added to improve the initial leveling and gloss. The amount of resin used in such products is not large at present because the exacting performance requirements make the development of satisfactory finishes containing large proportions of resin extremely difficult. Quick-drying house paints possess very definite advantages such as a reduction in the danger of impairment of the appearance of the film from dirt, leaves, or sudden rain storms during the drying period. In order to be completely practical, however, such paints must brush well, must adhere well to any and all old paint, must maintain fairly flexible films which do not pull off previously applied paint coatings with contraction in drying, and must be somewhat permeable to moisture so that moisture in the wood behind the paint film will have a tendency to go out through the film rather than to cause blistering or flaking (1). Although many investigators are probably working on the problem, there are not many practical house paint body colors made with fortified vehicles meeting these requirements on the market at present.

Varnishes are quite widely used, on the other hand, in proprietary trim paints. In the first place, the type of wood and the condition of the old paint over which these products are used are generally better than on the main body of dwellings. In addition, trim paints are

usually applied to smaller surfaces and there is less danger of moisture behind the film causing poor adhesion since the water pressure, if any, can usually be relieved in other directions. Taking all these factors into account, however, there probably is a tendency toward somewhat greater ultimate cracking and flaking failure with fortified and enamelized trim paints than with those made with raw linseed oil.

The advantages to be gained, however, by the use of varnishes and bodied oils in trim paints are quite marked. By replacing the raw linseed oil used in ordinary oil paints with varying amounts of varnish, the extender which is necessary in oil paints to produce satisfactory durability and proper paint body may be correspondingly reduced. The result of this replacement is a marked improvement in the gloss, flow, and particularly the color retention of the paint. The drying time may also be reduced, the practical advantage of which has already been pointed out. The improved color retention obtained by reducing the extender content is the principal advantage to be gained by the use of fortifying varnishes. This improvement is considered by most technologists to outweigh whatever tendency the harder, more brittle films may have ultimately to promote cracking and flaking failure on substrata in poor condition for painting.

The most commonly used varnishes in trim-paint vehicles are the so-called long-oil alkyd resins of the linseed or soybean oil modified types. The reason for this is the outstanding gloss retention (5, 6) and resistance to chalking, checking, and cracking failure which the drying oil modified alkyd resins exhibit on exterior exposure.

Quite satisfactory trim paints may be formulated using a vehicle the solids portion of which is composed of 50 per cent of long-oil alkyd and 50 per cent of raw linseed oil. Such a vehicle has much better gloss retention on exposure than raw linseed oil, approaching the straight long-oil alkyd resin in this property, while retaining much of the excellent brushability of raw linseed oil. The formulation of trim paints from this vehicle is fairly simple in most colors. The prime pigment needed to obtain the color and hiding required when incorporated in a vehicle as indicated above usually yields a paint of satisfactory working properties. If the body of the paint is too high it may easily be adjusted by the addition of thinner. If too low, a small amount of extender may be added or some of the raw oil may be replaced by kettle-bodied oil. The latter procedure is to be preferred, since, in general, better color retention is obtained by keeping *all* extender out of trim-paint formulations. Vehicles consisting of

combinations of alkyd resin, with raw and bodied oils, should always be pretested without pigmentation to make sure of their miscibility.

### PIGMENT CONCENTRATION

The general experience of numerous investigators has indicated that in white and light-colored house paints a fairly definite optimum exists as regards pigment concentration in the neighborhood of 28 per cent of the total volume of the non-volatile ingredients in the formula. The customary practice in house-paint formulation is to maintain the total concentration of pigment plus extender fairly close to this point since poorer durability or other performance characteristics are encountered at higher or lower pigment concentrations.

No such definite pigment volume is necessary or desirable in trim paints although the lighter tints, especially those high in raw linseed oil, will tend to approach it.

The darker tints as well as all the solid-color trim paints should be formulated to meet the performance requirements previously discussed in this paper without regard to the maintenance of any particular pigment concentration either by weight or by volume. The reason for this is that the various-colored pigments used in trim-paint formulation differ so widely in hiding, paint-thickening power, and particle size that it is doubtful whether there is any relationship between them as regards optimum concentration.

Since it probably has only slight significance, the pigment volume of trim paints is seldom calculated. Ordinarily, the pigment concentration is expressed in pounds per gallon or percentage of the total formula from which, knowing the gallon weight, the cost of the formula may easily be calculated.

The usual practice in pigmenting trim paints is to use enough pigment to obtain the hiding required and then to adjust the consistency of the paint with extender or vehicle variations as discussed previously. Trim paints in a few colors such as blacks, browns, and solid-color greens are generally pigmented somewhat higher than the minimum hiding-power requirements for reasons which will be discussed later.

### EXTENDERS

It has been pointed out that paints pigmented with combinations of C.P. colors and extenders have a tendency to fade more than paints made with C.P. colors alone. In spite of this, extenders are widely



used in raw linseed and fortified trim paints to produce proper body and eliminate running.

In house paints, the best extender is generally considered by most authorities to be properly chosen fibrous magnesium silicate. Experience has proved that in paints of this type magnesium silicate generally produces excellent resistance to checking and cracking as well as reasonably satisfactory fading resistance in the tints compared with other types of extenders. It also has very high paint-thickening power and excellent settling resistance as well as other desirable characteristics.

Magnesium silicate is also widely used in trim paints since the properties which make it valuable in the white and light-colored house paints are equally applicable in the darker trim paints.

Many of the diatomaceous and other types of amorphous silica make effective extenders for trim paints. These extenders vary widely in paint-thickening power, depending largely on differences in oil absorption. The very high oil absorption diatomaceous silicas may be blended with barytes in various proportions to produce practical extender combinations.

#### PIGMENTATION

Trim paints normally are applied at spreading rates of 500 to 700 square feet per gallon. Since application costs are high on account of the nature of the surfaces on which they are used, it is most desirable that they be formulated to give practical one-coat hiding at spreading rates of not less than 500 square feet per gallon. Even though the use of sufficient pigmentation to return such a hiding level may result in rather high material costs per gallon in certain colors, the total cost of the finished paint job to the householder will be lower if only one coat of trim paint is required.

#### Solid-Color Greens

The light, medium, and dark solid-color greens still make up the bulk of the trim-paint market although, as has been mentioned previously, various other colors are growing in popularity.

The solid-color green trim paints are generally made from chrome greens since these pigments are most practical for such products, taking into account all such factors as cost, hiding, gloss retention, and durability. In order to obtain superior resistance to color change other pigments, such as chromium oxide, chromium hydrate, or iron blue blended with zinc yellow or hansa yellow, are occasionally used.

While somewhat superior in resistance to color change, trim paints made with such pigmentations are usually higher in material cost at equal hiding levels as well as inferior in gloss retention and general durability to products made with chrome greens.

The lightfastness of solid-color trim paints made with chrome greens improves somewhat with increased pigment concentration (3). For this reason they are almost invariably formulated at considerably above the hiding level stated above of 500 to 700 square feet per gallon. A fairly satisfactory compromise between cost and lightfastness may be obtained by pigmenting the light greens at about 2 pounds per gallon, the medium greens at 1½ pounds per gallon, and the dark greens at 1 pound per gallon. Such pigment concentrations give trim paints with considerable excess hiding power but returning a reasonable degree of resistance to color change.

### Green Tints

This class of colors includes the so-called jade or emerald greens which are becoming quite popular. They all contain varying amounts of white pigment, which complicates the formulation of durable goods in these shade ranges quite materially. In order to obtain the weathering properties which are desirable in high-quality trim paints, careful selection of both the white and colored pigments included in the formulation must be made. White pigments of maximum chalk resistance are required as well as permanent tinting pigments. Chrome greens, while generally satisfactory when little or no white pigment is present, tend to fade out in tints containing appreciable quantities of white.

Chalk-resistant titanium dioxide, lead titanate, antimony oxide, or properly selected zinc oxide are among the most suitable whites for use alone or in combination in these products. Jade green trim paints having one coat hiding at spreading rates of 500 square feet per gallon may be formulated with all these white pigments.

There is a considerable difference in the chalking resistance of various types of titanium dioxide and zinc oxide and they should therefore be selected on the basis of exposure tests for use in trim paints. In general, the large particle size zinc oxides such as the acicular types are better in chalk resistance than the finer grades.

Paints containing zinc oxide and at the same time vehicles high in hard-drying varnish content may give trouble from excessive bodying and may also develop poor film durability on certain surfaces, particularly low-grade woods or old paints in comparatively poor

condition. They should therefore be subjected to storage tests to determine their package stability, and their exterior weathering characteristics should be established by actual service tests before being marketed.

Among the permanent tinting pigments useful for the formulation of high-grade green tints are:

- Copper phthalocyanine green.
- Hydrated chromium oxide (Guignet's green).
- Copper phthalocyanine blue and zinc yellow.
- Vat dye blues and zinc yellow.
- Chromium oxide.

The above colors are listed in approximately the order of brightness of the tints produced. The zinc yellow is, of course, used to control the amount of blueness or yellowness desired. It could, of course, be blended with the copper phthalocyanine green, Guignet's green, or chromium oxide if it is desired to produce yellower tints than may be obtained from the green tinting pigments alone.

Chrome yellows and certain types of organic yellows may also be used in green tints, although as a general rule they are not as satisfactory as zinc yellow. The organic yellows are expensive and must be selected on the basis of exposure tests since they vary widely in performance characteristics. The chrome yellows are less expensive than zinc yellow but green tints containing them have a tendency toward poorer lightfastness.

It is impossible to offer even approximate suggestions as to pigment concentration and proportions in green tints since the pigmentation varies widely, depending upon the shade and hiding power desired. In general, *tints* tend to *fade less* when pigment concentration is *decreased*. It will be noted that this is exactly opposite to the behavior of solid colors, which usually tend to develop *more color change* as the pigment concentration is *decreased*. Tints, therefore, should be formulated at a hiding level close to the lower limit which has been mentioned previously of 500 square feet per gallon.

Jade green trim paints may in some cases have fairly high material costs owing to the use of expensive tinting pigments. Material costs may be lowered considerably without sacrificing durability or hiding by the addition of a small amount of black tinting pigment such as lampblack. This reduces the brilliance of the product but it also boosts the hiding so that the total pigment content in the formula may

be materially reduced while the hiding is maintained at the 500 square feet per gallon level.

### **Blacks**

Black trim paints should be made with carbon black as the base pigment on account of its jetness and gloss retention compared with other black pigments. The lower-cost carbon blacks on the market are generally entirely satisfactory. For satisfactory package stability in paints containing large proportions of linseed oil, mineral blacks or iron oxide blacks which act largely as extenders are used in practical formulations in addition to a certain amount of suspending extender to prevent hard settling.

The enamelized black trim paints may be made with straight carbon black without other pigments if desired. In black automotive enamels and lacquers which are made with the very highest grades of carbon blacks, a considerable proportion of properly chosen iron blue is used to increase jetness on exposure and to promote drying. Black trim paints may also be improved in a similar manner by the admixture of iron blue pigment.

The pigmentation of black trim paints is generally rather inexpensive so that as a rule their hiding is much higher than that of some of the other colors.

### **Browns**

The brown trim paints used for the most part on English-type houses are generally made from iron oxide pigments suitably blended to match the shade desired and with extender added, of course, in formulations high in raw linseed oil. A small amount of durable organic maroon is sometimes added to such products to give a little more warmth to the color.

### **Light and Medium Blues**

These products may be considered together since no sharp line of demarcation exists between them. The blues are probably the most difficult to formulate of all the trim-paint colors as regards permanence of tint. Copper phthalocyanine or vat dye type blues are far superior to other types in color retention but the white and the vehicle used play an important part in establishing the durability of the product.

The white pigments used in these products are the same as for the jade or emerald green shades discussed above. Like the latter, the

hiding should be adjusted to not greatly above the 500 square feet hiding level for best control of fading.

Black tinting pigments may be used with blue to reduce material costs. The corresponding reduction in brilliance is often considered desirable in blue trim paints since the copper phthalocyanine blues particularly produce tints which are brighter than required by many consumers.

### Dark Blues

Lightfast dark blues, like the lighter shades, also present serious formulation problems. Large proportions of the copper phthalocyanine and vat dye blues in trim paints run up the material cost rapidly and involve certain other difficulties such as poor leveling characteristics. This is particularly true with the phthalocyanine blue, which also has a tendency to bronze on exposure in dark tints. Iron blue is, perhaps, the most satisfactory pigment for dark blues with or without a proportion of the above pigments to improve the lightfastness.

Since iron blue is a semi-sensitive pigment as regards lightfastness in tints, white pigments, such as the zinc oxides, which produce the least chemical fading, must be used to produce the particular shades desired.

### Maroons

Maroon pigments for use in trim paints must be bright, strong, have good hiding, and must be permanent both when used alone and when blended with iron oxides or other permanent pigments. There are several maroon pigments on the market which meet these requirements. About  $1\frac{1}{2}$  pounds of maroon pigment would be required to produce a trim paint of 500 square feet hiding when used alone. They may be blended with as much as 50 per cent of bright iron oxide, however, without a great deal of reduction in brightness. The oxide boosts the hiding so that less than  $\frac{3}{4}$  pound per gallon of the expensive maroon pigment is required.

### Bright Red

Toluidine red is an exceptionally good pigment for use in trim paints of this depth of shade. Its lightfastness, durability, and general pigment properties are among the best of the organic red pigments. About  $1\frac{1}{2}$  pounds would be required for 500 square feet hiding when used alone. Blends containing up to 25 per cent of bright synthetic iron oxide are somewhat softer in tone and more pleasing than the

straight toluidine red while requiring not more than 1 pound per gallon of the latter at a satisfactory hiding level.

There are other organic red toners available similar in shade to toluidine but of a proprietary nature which would be even more suitable than toluidine in a trim paint of this shade range. The main advantage of properly selected toners such as those mentioned is that in blends with yellow to make oranges or with maroons to make dark reds they are even more lightfast than similar shades made with toluidine red.

### Yellows

The chrome yellows would seem to be the most practical for yellow trim paints in spite of a tendency to darken. They are moderate in cost and higher in hiding than any of the other yellow pigments which might be used in such products. Using C.P. chrome yellow medium, approximately 4 pounds per gallon is necessary to attain 500 square feet hiding in a trim paint, although, by blending with a bright synthetic yellow iron oxide or chalk-resistant titanium dioxide, this amount could be materially reduced. Very attractive yellow trim paints of good durability and low cost may be formulated from combinations of white, chrome yellow, and iron oxide yellow.

There is a demand for yellow trim paints for such special purposes as finishes for store fronts and gasoline service stations as well as for dwellings. As mentioned above, properly formulated yellow and bright red trim paints may be blended to produce attractive and durable oranges in a wide range of shades.

### UNDERCOATS FOR TRIM PAINTS

Many paint manufacturers market special undercoats made up in gray or other neutral colors as primers for trim paints on wood since these undercoats are generally cheaper and better as primers than the trim paints.

Suitable formulations for this purpose are the primers developed for two-coat house-paint systems (4). These primers have much higher pigment volumes than trim paints (around 40 per cent) and are made with vehicles having controlled penetration. They therefore have much better build, sealing, and filling properties and when covered with one coat of trim paint produce finishes of better appearance and durability in many instances than do two coats of trim paint alone.

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## CHAPTER 11

### PAINTS AND ENAMELS FOR INTERIORS

ROY E. TROUTMAN

The art of paint making is many centuries old. The ancients' practice of daubing their bodies with various-colored earths mixed with fats or greases probably marks the earliest use of paint pigments.

The history of pigments used in the manufacture of paints is closely related to that of varnishes in so far as their concurrent development is concerned. The manufacture of varnishes has probably been continuous since the time when the Egyptians varnished the cases in which they enclosed their mummies, some 2,500 years ago.

The use of pigments for ornamental purposes is probably one of the oldest forms of decorative art. Many of the materials used, especially various forms of earth deposits, were available to the artist without any special preparation. Furthermore, various pigments have been used in protective coatings of some form or other for many years. White lead, for instance, was mentioned in the writings of Theophrastus as early as 400 B.C.

The utilization, therefore, of various pigmented paint systems as protective and decorative coatings is of great and relatively unknown antiquity. Ever since their inception, paint and enamel coatings have gradually increased in utility to a point where they now serve innumerable fields. Although even today paint making is probably more of an art than a science, tremendous scientific progress has been made in the last few decades. Through the efforts of research and development, great improvements have been made in raw materials and manufacturing methods which have resulted in vastly improved finishes and in the introduction of many new products. The discovery of these newer materials, finishes, and finishing methods has stimulated rapid expansion of the industry.

#### PAINT SYSTEM COMPONENTS

Paints and enamels may be regarded as systems comprised of pigments and vehicles as the two major components. The pigment con-



stituents may be further classified into prime or opaque materials (high refractive index) and extenders (low refractive index). The vehicle portion generally consists of a combination of oils, resins, thinners, and driers.

## PIGMENTS

### Prime Pigments

Inasmuch as the various pigments are completely described in Volume II, this discussion will be limited to their primary functions as related to paint systems. Prime pigments are characterized by a high degree of opacity, color, and brightness; consequently their primary function is to provide the required hiding power in a given paint system. There are a number of distinctly different types of prime pigments which vary significantly in color and hiding power as well as in other intrinsic properties. Their behavior in paint systems is subject to considerable variation depending upon the inherent nature of the pigments.

**Lead Pigments.** No space will be devoted to white lead pigments in this chapter, in view of the fact that these pigments are discussed in detail in the chapter on exterior finishes, Chapter 10A.

**Lithopone.** Lithopone has been used in the manufacture of paints and enamels ever since the early seventies of the nineteenth century. Its general utility soon became manifest by its wide acceptance in a variety of finishes. In recent years, however, it has decreased in usage because of the advent of newer types of pigments which have replaced it in many products by virtue of their having more suitable properties.

The many grades of lithopone available to the industry today differ primarily in their inherent physical and chemical characteristics. Oil absorption, consistency, reactivity, particle size, and opacity are among the most prominent properties and they frequently govern pigment selection for a specific system. Some of the lithopones carry a surface treatment in the form of an organic coating which facilitates wetting and improves suspension. The disadvantages of most of the surface treatments are that they frequently retard leveling and may result in slight gloss deficiencies, especially in the more critical formulations. The reduction in leveling may serve as an advantage in overcoming sagging difficulties.

Lithopone is a high density pigment of relatively low bulking value which permits its incorporation at fairly high pigment concentrations. Paints may carry 4 to 12 pounds of pigment per gallon, depending upon

cost, consistency, opacity, and gloss considerations. Flat paints will naturally tolerate a higher pigmentation than gloss paints and enamels. A high hiding lithopone flat usually contains 10 to 12 pounds of pigment per gallon, whereas enamels are prepared in a lower pigmentation range and contain approximately half this amount. The high oil absorption or thick consistency types are usually chosen for flat paints whereas generally the low or medium oil absorption types are used in gloss paints on account of their better gloss-producing properties. The latter are characterized by extremely fine particle size which enhances gloss, ease of dispersion and suspension, and therefore are better suited for gloss paints.

In general, lithopone paints have good drying properties coupled with good universal film properties and package stability. They lack hiding power, initial color, and brightness as compared with titanium pigments and show a greater tendency toward discoloration in the dark.

Within the last few years lithopones yielding increased dry film hiding power have been introduced into the industry. These types are characterized by high dry flat hiding and high consistency, and as a result are best suited for flat paint work. The high dry hiding is accompanied by low wet film hiding and a deficiency in certain film properties, particularly poor enamel holdout and washability. Some of these pigments are also highly water sensitive, which results in a great increase in body when water is added. These types are not amenable to general formulating work but are most advantageously confined to specific fields where high dry hiding is the primary requisite. Their use is largely restricted to flat paints and cold water paints by virtue of their low sheen characteristics.

The high strength lithopones (50/50-zinc sulfide/barium sulfate) and titanated lithopones (15/85-titanium dioxide/lithopone) are similar in general characteristics and behavior to the normal lithopones. They have been designed to yield greater tinting strength and opacity per unit of pigment and therefore are used to obtain higher hiding in products where the pigment concentration is limited by the other properties desired. Gloss paints, for instance, will accommodate a lesser pigment concentration than flat paints and therefore require pigments of greater inherent opacity to permit lower pigmentation without sacrifice in hiding power.

**Zinc Oxide.** Zinc oxide has been known to the industry for many years and has found wide acceptance principally because of its chemical and optical properties. Most types react readily with the acidic portion of the vehicle to form zinc soaps. These soaps impart various

properties to both the paint and paint film, depending upon the type and amount of soaps formed. Effects on such properties as consistency, degree of dispersion, suspension, gloss and gloss retention, color and color retention, and film hardness have been ascribed to the presence of these soaps.

Invariably the presence of zinc oxide in a formula will result in increased consistency, the degree depending upon the amount of zinc oxide present and the nature of the vehicle. Highly acidic vehicles are susceptible to excessive reaction. In most vehicles zinc oxide promotes flow, sometimes to the point of sagging, whereas in other vehicles the leveling properties may be retarded, which is the case when used with some of the alkyd vehicles or bodied fish oils.

Excessive amounts of zinc oxide may cause early film embrittlement due to their hardening effects. Conversely, some zinc oxide may be desirable as a means of improving film hardness as well as for enhancement of gloss and color retention. As a result small quantities are frequently used in conjunction with other prime pigments to impart specific properties.

Although the effects of reactivity and soap formation have long been recognized, the view has recently been proposed by Nelson (15) that many of these effects previously ascribed to the presence of zinc soaps are really due to the role of zinc oxide as a polymerization catalyst. It has been possible to distinguish between soap effects and polymerization effects in zinc oxide bearing paint films and to follow their progress. Polymerization changes in oleoresinous systems may frequently be desirable from the standpoint of resistance to various elements, whereas oxidation changes may produce undesirable results in the same film.

The consistency changes which occur in a paint due to zinc oxide reactivity are frequently referred to as "livering." See Chapter 4, Volume IV. The degree of livering is governed by the nature of the pigment with specific reference to surface activity, structure, and the acidic nature of the vehicle used. Vehicles play a very prominent part. Both the type and amount of acid present greatly influence the reaction. Newer types of zinc oxides can be used with the ordinary oleoresinous type of vehicle without excessive reaction. These are referred to as "non-reactive" types, and allegedly differ from the normal oxides primarily in particle size. Variations in particle size and reactivity make it possible to obtain a wide range of paint consistency. In addition to the effect which particle size and reactivity have on consistency, Nelson (15) also claims that the hydrophilic

nature of a zinc oxide surface could also be responsible for the development of a thixotropic state in the paint and offers this as a possible explanation for the generally good non-sagging qualities of enamels containing high zinc oxide content.

**Zinc Sulfide.** Zinc sulfide is a pigment of high refractive index yielding fairly high opacity. Prior to the advent of titanium dioxide it was the highest hiding white pigment used in the paint industry. Unlike zinc oxide, zinc sulfide is chemically inert and therefore is not subject to reaction with the vehicle. It has been very popular for use in cold water paints, principally because of high opacity, accompanied by chemical inertness, in casein vehicles.

**Titanium Dioxide.** Titanium dioxide is one of the newer types of pigment in the paint industry. It is available as commercially pure titanium dioxide and is manufactured in several different crystal forms. These crystal forms differ in their index of refraction, which is not an uncommon phenomenon. For instance, the well-known differences between the two forms of carbon known as graphite and the diamond are the result only of changes in crystal form.

The two crystal forms of titanium dioxide of immediate interest are called anatase and rutile. Anatase has an index of refraction of 2.53 and is the crystal form which has been on the market for several decades. Rutile, on the other hand, has an index of refraction of 2.71 and has been commercially available for only about a year. The higher index of refraction of the rutile crystal results in greater opacity.

The two types of titanium dioxide pigments also differ in inherent color characteristics. Visual inspection will generally show that rutile paint films are slightly more yellow than comparable anatase paint films formulated on the same basis. Spectrophotometric measurements show considerably lower reflectance for the rutile pigment in the violet end of the spectrum (400–430 millimicrons). However, at all wavelengths above 430 millimicrons the rutile crystal form shows higher reflectance than anatase. As a result rutile films observed in ordinary daylight will appear appreciably brighter and more yellow throughout the yellow and green range of the spectrum, where the human eye is most sensitive.

Greatly increased hiding power constitutes the outstanding property of the rutile titanium dioxide pigments. Usually they exhibit about one-third greater opacity in comparison with corresponding anatase grades. Actually the improvement in hiding power may range from 20 to 50 per cent greater, depending on the system in which they are

used. Quite obviously the greater inherent opacity of the rutile pigments is reflected in possible savings in raw material cost, which are quite significant.

In all other properties the rutile and anatase pigments are quite similar and may be discussed as a group.

The principal advantage of the pure titanium dioxide pigments lies in their exceptional opacity, which is the normal result of their high refractive indices. Other outstanding characteristics are color, brightness, and color retention. Because of these properties these pigments have found wide usage in high quality finishes. Such pigments are particularly well suited for use in products where high pigment concentration is precluded because of gloss, consistency, and application requirements. Yet, because of their inherent opacifying power, maximum hiding power effects may be obtained with minimum amounts of pigment per gallon of paint.

The titanium dioxide pigments are inert chemically and can therefore be used in almost any type of paint vehicle or other binding medium without danger of chemical reactions taking place with corresponding changes in the physical properties of the paint.

Titanium dioxides are being consumed in a wide diversity of finishes. Many architectural paints and enamels made from synthetic resin vehicles of either air-dry or baking types as well as nitrocellulose coatings are based on these pigments. Such commodities usually contain  $2\frac{1}{2}$  to  $4\frac{1}{2}$  pounds of pigment per gallon of paint, depending upon hiding power requirements and other properties desired. Low pigment concentration is advantageous in finishes using high viscosity liquids where a high pigment content would produce finishes with too heavy consistency to be practical. Through the use of titanium dioxide, finishes can be produced at low consistency suitable for brushing or spraying and at the same time possessing high hiding power.

Paints containing titanium dioxide frequently lose drying efficiency on aging. This is attributed to drier adsorption and in many cases may have to be corrected by making an adjustment of the drier. Frequently the addition of slightly excessive amounts of selected driers to the original paint will adequately diminish the loss of drying on prolonged standing.

In addition to its almost exclusive use in high quality synthetic finishes, titanium dioxide has also found very wide usage in numerous other coatings made from non-synthetic oleoresinous vehicles. In the latter type, it may be used as the predominating pigment or in conjunction with other pigments, to augment the hiding power of the

system. Its properties make the pigment both suitable and desirable for almost any type of system.

Various grades of titanium dioxide are also used in the manufacture of extended pigments in which the titanium dioxide exists in combination with suitable extenders. The extended pigments differ primarily in so far as the extender portion is concerned and the grade of titanium dioxide employed. Generally the titanium dioxide is combined in a 30/70 ratio by weight with the different extenders—barium sulfate, calcium sulfate, and magnesium silicate.

**Titanium Barium Pigment.** Titanium barium pigment is a high density, low bulking pigment of good color and opacity and possesses good gloss-producing properties. It is a non-reactive pigment which contributes good flow, leveling, and gloss to a given system. It is used extensively in both interior and exterior finishes, the latter of which are covered in detail in Chapter 10A. This pigment is suitable for products such as undercoaters, quick-drying enamels, and floor enamels. By virtue of high density it shows a greater tendency toward settling than some of the other pigments.

Titanium barium pigment is available in several grades. The normal grade is intended for use in general formulating work involving the usual oleoresinous vehicle systems. Another grade gives excellent dispersion in water media and is primarily intended for use in cold water and emulsion paints. A third grade available carries a surface treatment which results in good suspension in certain modified phenolic resin liquids where lack of suspension normally presents difficulties. Other grades are also available, made with chalk-resistant types of titanium dioxide, which impart additional properties to the paint.

By virtue of its low bulking value, titanium barium pigment permits relatively high pigmentation at fairly low paint consistency. Formulations may range from 4 to 7 pounds of pigment per gallon, depending upon the hiding power requirements of the finished product. The grade selected is governed by the inherent properties desired in the paint.

The titanium calcium pigments differ in properties from the titanium barium pigments principally because of the different type of extender used.

**Titanium Calcium Pigments.** Prior to the advent of rutile titanium dioxide the use of calcium base titanium pigments was confined primarily to interior finishes. Since the introduction of rutile, titanium calcium pigments which are suitable for exterior use have been made available to the industry. These are discussed in Chapter 10A. The

present discussion will be restricted to the grades intended for interior finishes.

The pigments used in interior coatings may be divided into two general classifications consisting of rutile titanium calcium and anatase titanium calcium pigment in which the words rutile and anatase simply define the type of titanium dioxide used. The former is characterized by increased opacity.

The exceptionally high hiding power of rutile titanium calcium pigment is not dependent upon a paint film surface effect often called "high flat hiding." It is dependent rather upon the fact that rutile titanium calcium carries approximately 30 per cent of rutile titanium dioxide. In fact, one of the most important features of rutile titanium calcium pigment is its ability to yield exceedingly high opacity paints without resorting to the use of additional titanium dioxide or without invoking "high flat hiding" effects with the consequent sacrifice in film integrity properties. It should also be mentioned that the value of rutile titanium calcium pigment increases as the desired hiding power level rises. Not only is it impossible to reach the higher hiding power levels with the anatase pigment but its hiding power efficiency at the higher pigment concentrations is also lower than that for the rutile pigment. This relationship in hiding power, however, will not remain constant. It has been observed that the advantage of the rutile titanium calcium pigment diminishes at pigmentations where "high flat hiding" becomes progressively more influential. In the average paint system, however, rutile titanium calcium pigment will show approximately 33 per cent improvement in hiding power over anatase titanium calcium pigment.

Titanium calcium pigments have found extensive adoption in numerous interior finishes such as undercoaters, primer-sealers, flat paints, gloss paints, enamels, mill whites, as well as many other products. They may be used as the sole prime pigment or in conjunction with other prime pigments and suitable extenders. The amounts used depend upon hiding power requirements of the finished product and economy restrictions. When using the anatase pigment the pigmentation usually ranges from 4 to 8 pounds of pigment per gallon of paint. The latter concentration produces paints in the high hiding range while the former yields systems of correspondingly lower hiding power. When using the rutile pigment only 75 to 80 per cent would be required to produce comparable hiding results.

Anatase titanium calcium pigments are available in a number of grades which differ in such properties as oil absorption, consistency,

and water sensitivity, thus affording a wide latitude for control of finished paint consistency as well as certain film properties. Pigments of fine texture are advocated for use in gloss paints and enamels. Through their ease of dispersion maximum gloss and film fineness can be obtained with a minimum amount of milling.

Other grades of titanium calcium pigments yield extremely "high dry flat hiding" in flat paints. These are mostly high oil absorption products which are hydrophilic and are therefore inclined to be excessively sensitive to water in poor wetting vehicles. Consistency due to water sensitivity may be controlled by selecting vehicles of proper wetting efficiency and moderate acidity.

**Titanium Magnesium Pigment.** Titanium magnesium pigment is used predominantly in exterior house paints and is discussed in detail in Chapter 10A. In interior finishes its use is limited to flat paints, where it may constitute a portion of the prime pigment as a means of sheen control. If used in excessive proportions it will detract from the color, hiding power, and leveling.

### Extenders

The term extenders as applied to paint relates to a class of compounds which serve a very useful purpose although their precise action is very difficult to define or explain. They fall into the group of low refractive index materials (refractive indices similar to oleoresinous vehicles) and as a result do not contribute to the opacity of a paint film. The very nature of some paint finishes prevents the use of any extenders, as typified by high gloss, high hiding enamels which as a rule do not tolerate more than the necessary amount of prime pigment. In other finishes their utility is well recognized from the standpoint of controlling various paint properties as well as the raw material cost. Selection of suitable extenders usually facilitates the control of consistency, brushing, leveling, sheen, and suspension. The type and amount selected depend entirely on the nature of the product and the distinctive features desired.

Commercially available extenders differ widely both in chemical composition and inherent physical properties. Furthermore, substantial variations in physical characteristics exist in products belonging chemically to the same family. Each class of compounds possesses individual characteristics which may vary within the group.

**Calcium Carbonate.** Calcium carbonate (whiting) is used extensively as a portion of the pigmentation in a wide variety of interior finishes. Its predominating use is in flat paints where it may consti-



tute 10 to 40 per cent of the total pigment plus extender content, depending upon the quality of the product. The selection depends upon such basic differences as color, oil absorption, particle size, and reaction. Alkali potential is a very definite factor in the control of paint properties. The presence of water-soluble alkali is conducive to the formation of reaction products which are influential in the control of paint consistency.

Some whittings are complex in chemical structure, consisting of calcium carbonate in combination with magnesium and aluminum compounds. The general behavior and function of these products are very similar to normal calcium carbonate and they are used in a similar manner.

Still another grade of pure calcium carbonate is surface-coated with a uniform layer of interactive material. When this product is dispersed in liquid media the interface does not present calcium carbonate to the vehicle compounds, but rather a complex organic structure having extraordinary tenacity in contact with those vehicle compounds.

Benefits arising from the excellent "wettability" of this material are the increased pigment concentrations which paints can carry and still not disturb established standards of consistency, luster, flow, leveling, and brushing. Higher pigment loading yields greater opacity and results in greater economy.

This material serves as a very efficient tool in the control of penetration and "hold-out" properties of pigmented sealers and undercoaters by virtue of its unique properties. The amount used depends on the type of formulation involved and the properties desired. In many formulations as much as 3 pounds per gallon is not excessive for base coatings whereas for finish coats the top limits will be defined by color limitations.

A calcium carbonate of colloidal fineness has been introduced recently which has been found very useful in the control of pigment floating and sagging tendencies.

**Magnesium Silicate.** Magnesium silicate (asbestine) is composed of more irregularly shaped crystals than calcium carbonate and is more fibrous in nature. It possesses relatively poor wetting properties as compared with whiting, and consequently it is far more difficult to disperse in the various vehicle systems. By virtue of this poor wetting, coupled with high oil absorption, the presence of asbestine in a paint tends to give increased body. At the same time the system is more sensitive to the various bodying agents. Asbestine is quite effec-

tive in lowering the sheen of flat paints and is frequently used for this purpose. If used in excessive amounts it will have an adverse effect on brushing, leveling, and color. Because of its coarse particle size asbestine is not suitable for use in gloss paints or enamels; however, it is frequently used as a means of controlling the sheen of semi-gloss paints and eggshell finishes.

Other modifications of asbestine consist of combinations of aluminum and magnesium silicates in varying proportions. These products are sold under various brand names, are similar in properties to the straight magnesium silicate, and are used in a similar manner.

**Silicon Dioxide.** Silicon dioxide (silica) exists in both crystalline and amorphous forms. It is a hard, abrasive type of extender which is used rather extensively in sanding sealers, surfacers, and undercoaters. It frequently improves the drying properties of a product as well as the ease of sanding. By virtue of its decided abrasive action it normally presents grinding difficulties which restrict its use to base coatings. It is inert chemically, and its coarse texture also makes it suitable as a flattening agent.

Another type of extender belonging to this group is diatomaceous silica. It is a white, fluffy material of very high bulking value and is used rather extensively as a flattening agent in paint systems. By virtue of its amorphous, diatomic structure it serves as an efficient tool in controlling sheen to any degree down to a dead flat. Its aid to suspension and its high light reflection in the dried films are additional attributes of merit. It has high oil absorption as well as a rather pronounced effect toward increased consistency. It is chemically inert. Relatively small percentages are normally sufficient to lower the sheen significantly.

**Barium Sulfate.** Natural barium sulfate (barytes) and blanc fixe, a precipitated product, are used in some interior finishes such as primers and undercoaters. These extenders are high-density, low-bulking materials with relatively easy wetting characteristics and are usually used in combination with other extenders. Chemically they are inert and permit high pigment loading without an excessive increase in consistency. This type of extender has relatively poor suspension properties, and as a result may cause excessive settling in the paint. The essential difference between the natural and precipitated products is color and fineness with the blanc fixe excelling in both these properties.

**Clay.** Other types of extender of more indefinite composition are the clays, both domestic and foreign. These products are usually

characterized by poorer color and texture, and they are not used as extensively in interior finishes, especially where color and film fineness are important. Their hydrophilic nature makes them highly suitable for use in cold water paints or any coatings of the emulsified type.

**Calcium Sulfate.** Anhydrous calcium sulfate is a more recent innovation. It is a precipitated product of relatively high bulking value, good color, and fine particle size.

Consulting Tables I and II may serve to clarify further the general classification of the prime pigments and extenders just discussed. These tables are self-explanatory and may facilitate proper selection of pigments for the individual problems.

### VEHICLES

The vehicle component of a paint system is generally composed of oils, resins, thinners, and driers. The solid portion, consisting of oils, resins, or both, constitutes the binding medium which has a predominating influence on package stability, ease of brushing, drying time, and all major film properties. The thinner portion serves as a diluent or solvent for the oleoresinous portion and is used primarily to reduce the latter to working consistency. Thinners also may have a significant effect on drying time. Driers serve as catalysts which accelerate the oxidation or drying action of the paint films.

Inherent characteristics of individual vehicle ingredients are discussed in detail in other chapters in Volumes I and III. Only their major influence in so far as paint properties are concerned are considered in this discussion.

### Varnishes

Varnishes and their related products exert a predominating influence on the chemical and physical properties of paint systems. Consideration of some of the basic functions of various ingredients may serve as a material aid in the proper selection of vehicles for the finish intended.

Limed rosin and ester gum are used very extensively throughout the industry in the form of spirit varnishes or in combination with various oils. These combinations may consist of cold blends in the paint or cooked vehicles of various oil lengths. The limed rosin products are frequently characterized by high acidity and are reactive with basic pigments. They are not only poorer in color initially but

also have poorer color retention than the ester gum vehicles. This relationship exists regardless of the pigmentation involved.

The presence of resin acids enhances the wetting and dispersion properties of a vehicle. At the same time rosin acids also favor increased body due to water sensitivity, especially when used with pigments which are sensitive to water. Ester gum products possess better initial color and color retention. By virtue of lower acidity and good wetting characteristics they are much less likely to yield increased body when water is added to the paint. Although they exhibit less residual tack in the dried film, some ester gum blends show a decided tendency to surface-dry, leaving a soft film underneath the surface.

In general, phenolic resin vehicles have a tendency to yield harder films with greater water and chemical resistance coupled with better durability. Usually phenolic resins yield varnishes of high acidity which makes them highly reactive with many of the basic pigments, resulting in increased consistency. Most phenolic vehicles are characterized by poor initial color and poor suspension properties. Furthermore, they lack good color retention especially in white products. The discoloration on aging of pigmented systems can be governed by proper pigment selection.

Alkyd resins as a class, when pigmented, show outstanding advantages in initial color and color retention. They yield very pale films in either air-dry or bake finishes. These resins also possess the additional feature of yielding good gloss and gloss retention, but some of them have the disadvantage of inferior application properties as compared to the phenolic systems. At the same time the films do not show the same degree of water and chemical resistance as phenolic vehicles.

Maleic anhydride resins are characterized by good color and color retention and as a result are used extensively in interior coatings, where these properties are important.

Other types of resins of more recent origin are also finding application in interior coatings. The terpenes and pentaerythritol resins belong to this group.

## Oils

As far as influence on paint properties is concerned, the various oils used for compounding may be classified into groups of raw, refined and bodied oils.

Raw and refined oils are characterized by low viscosity, easy brushing, poor leveling, slow drying, and relatively low gloss. The refined oils differ from the raw oils essentially in better initial film color and better color retention regardless of the pigmentation employed. The different kinds of oils will also vary in color and color retention with soybean oil excelling, followed by perilla, linseed, and fish. The proportion of unkettled oils which can be used in a given system is governed by such properties as consistency, brushability, leveling, and drying time. Usually a compromise has to be reached between bodied and unbodied oils in order to take advantage of all the desired properties.

Kettle-bodied oils may vary decidedly in characteristics, depending upon the type of oil, the method of processing, and the final degree of oxidation or polymerization attained. Bodied oils possess better wetting properties, promote more flow, and have better drying properties and color retention than the unbodied oils. They are decidedly poorer brushing than the unbodied oils, the adverse effect being directly proportional to the degree of polymerization.

Blown oils are noted for their excellent wetting properties. As a class they are significantly better in this respect than the kettle-bodied oils, which in turn are better than the unbodied oils. Inasmuch as degree of wetting influences flow and leveling, this property may lead to sagging difficulties if not properly controlled. Furthermore, blown oils, in unlimited proportions, are not always compatible with the remainder of the vehicle because of package instability. As a factor of safety, no more than 25 per cent of the vehicle solids as an absolute maximum should consist of blown oil. Frequently it is advisable to use a small percentage of a high solvency thinner such as dipentene or high solvency mineral spirits in conjunction with the blown oil to insure better stability and compatibility.

Bodied perilla, linseed, and soybean oils promote good flowing properties and in this respect are much better than the fish oils of comparable viscosity. Bodied fish oil is characterized by poor flow and may be used to retard leveling sufficiently to control sagging. The use of zinc oxide with bodied fish oil offers a further restriction on flow. Up to certain limits the flowing properties of these oils are directly proportional to the viscosities of the oils.

Linseed and soybean oils will generally produce slightly better gloss than perilla, whereas fish oil is definitely inferior in this respect. Excessive amounts of fish oil will produce rapid loss of gloss in the film, especially under hot, humid conditions. At the same time bodied

fish oil will yield notably greater ease of brushing than the other oils at comparable consistency. In each case the application properties are inversely proportional to the viscosities of the oils.

Other oils such as hempseed, safflower seed, and corn oil have also found limited use in paints and enamels as partial replacement for some of the oils just mentioned.

There is still another group consisting of oiticica and dehydrated castor oils which has found application as partial replacements for tung (China wood) oil. The introduction of these softer drying oils, including linseed and perilla, coupled with the necessary resin reinforcements, has resulted in vehicles of greater wetting efficiency. In many instances this has led to thinner paint consistencies accompanied by poorer suspension and has accentuated flowing properties sometimes to the point of sagging.

### Thinners

Thinners constitute the other major vehicle constituent. Solvents such as mineral spirits, "Varnish Makers' and Painters' Naphtha" (V.M.&P.), turpentine, kerosene, dipentene, high solvency petroleum thinner, heavy mineral spirits, pine oil, and various coal tar hydrocarbons are used rather extensively in the paint industry. These solvents differ primarily in solvent power and rate of evaporation, two factors which have a pronounced influence on ease of brushing, leveling, drying time, and lap time of a given paint system.

Mineral spirits evaporates at a faster rate than turpentine and has a less pungent odor; however, it has lower solvency. For faster set-to-touch time, V.M.&P. naphtha may be used. It evaporates at a rate appreciably faster than regular mineral spirits. The high solvency petroleum thinners have higher solvent power than regular mineral spirits. The various grades available differ primarily in initial boiling point and distillation range.

Kerosene has relatively low solvency and evaporates at a significantly slower rate than mineral spirits. This makes it a very useful constituent to prolong lap time, and it is therefore useful for the control of brushing properties by appropriate blending with other thinners.

Dipentene is a high solvency thinner which evaporates at a significantly slower rate than mineral spirits. Its relatively high solvency limits its use to approximately 15 per cent by weight of total thinner in most common formulations. Quantities in excess of this amount

may cause lifting of the first coat when the second coat of paint is applied.

The coal tar hydrocarbons are high solvency thinners and are used primarily in products where the aliphatic hydrocarbons are of inadequate solvency to effect solution and compatibility. The rate of evaporation of the low flash types is relatively fast, which limits their use to spray application predominately. Some of the synthetic resins require the higher solvency thinners to insure compatibility and effect greater reduction in viscosity per unit volume of thinner added. The thinner or combination of thinners selected will be governed by the type of resin involved and the properties desired in the finished paint.

Small amounts of pine oil may be used to improve ease of brushing and prolong the lap time or set-to-touch period. Large percentages are not recommended because of its adverse effect on drying time and film hardness.

According to Krumbhaar (10), the presence of peroxides such as are found in oxidized turpentine, pine oil, dipentene, and several high solvency petroleum thinners intensifies the efficiency of driers, although the peroxides do not themselves act catalytically in the absence of drier metals. Their effect depends upon the amount of peroxide oxygen present. This may also be responsible for the development of greenish tints in white paints containing such thinners. Cobalt in the divalent state is blue, which in the presence of these peroxides may oxidize to the trivalent state, which is green. Peroxides contained in linseed oil may behave similarly.

### Driers

The metallic salts used as driers constitute the third vehicle constituent influencing paint and film properties. Their main function is to accelerate the rate of drying of a film. The transition from the liquid phase to the solid phase involves a combination of oxidation and polymerization. The driers act as catalysts which hasten these processes, which may actually progress to the final disintegration of the film.

In a theoretical discussion Stephens (23) points out that the action of catalysts (driers) on the oxidation of drying oils is not due to any direct catalytic speeding up of the oxidation process but to the driers in some way inhibiting the action of natural antioxidants. This hypothesis is supported by the fact that the maximum oxidation rate of such oils is little affected by the addition of antioxidants or driers and also by the fact that superpurification of simple compounds greatly

speeds up their oxidation. Energy released by the oxidation of drying oils promotes their polymerization by furnishing the necessary activating energy.

Lead, manganese, cobalt, and zinc metals combined with various acid radicals constitute the most commonly used driers. The main function of these metal salts is to accelerate drying, and their effect on rates of drying and on various paint properties will vary according to the type of drier employed. The three types most commonly used consist of resinates, linoleates, and naphthenates, which may vary in their influence on consistency and package stability.

The efficiency of one drier metal may be intensified by the presence of another; consequently combinations of metallic driers are usually employed to produce the most effective results. Within limits, the drying efficiency is directly proportional to the quantities of metals present, which is usually expressed as percentage metal based on total weight of oil. Practical considerations such as film thickness may limit the maximum amounts to be used because of wrinkling and other film malformations during the drying process, as well as the danger of skinning in the can. Excessive amounts of cobalt and manganese have adverse effects on initial color and color retention, manganese being the worse offender. The use of soluble lead driers with some types of alkyd resin may result in the precipitation of lead phthalate with corresponding loss of drying strength and lower gloss. This tendency is accentuated by the use of excessive amounts of lead drier.

Soluble zinc and calcium compounds, which by themselves do not act as driers, produce an accelerating effect when used in combination with driers. They are commonly used in this manner. Zinc in the form of naphthenate or resinate has been used rather extensively with greatly accelerated drying action, especially when used in conjunction with cobalt, manganese, or both. The presence of the zinc improves the drying efficiency and results in greater ultimate hardness. Calcium when introduced as a soap produces similar effects. A convenient way to introduce calcium is in the form of limed rosin, although the naphthenates are preferable to the resinates by virtue of their having better color retention. Both zinc and calcium are sometimes used to delay the initial "set-to-touch" time of paint films and to prevent incipient wrinkling.

Iron salts are sometimes used to harden films, especially in bake finishes. They are restricted to use in dark-colored products, how-



ever, because of their dark color and their discoloring tendencies on the film.

### Soaps

Non-siccative metallic soaps, including stearates, palmitates, naphthenates, and oleates of aluminum, calcium, and zinc, are frequently used as suspension aids and to produce desired flattening effects. Of these, the aluminum stearate is most commonly used. It may be incorporated in the dry state or in the form of a gel in mineral spirits. Where suspension is of primary importance it is preferable to use the gel for maximum efficiency whereas the dry powder is usually more efficient as a flattening agent. These soaps have also been found to be effective in the control of pigment floating and paint sagging tendencies.

These materials differ in chemical and physical characteristics which govern their influence on various paint properties. Most of them will show a tendency toward increased paint consistency and reduced leveling. Their use in gloss paints and enamels is restricted by their adverse effect on gloss. Conversely, they are frequently used in flat and semi-gloss paints as a means of controlling sheen and gloss. In flat paints their presence usually accentuates the water sensitivity of the system and enhances the ease of brushing. Individual behavior and specific properties desired in the finished paint govern the selection of the type and amount to use. For general work, quantities up to 1 per cent, based on the weight of total pigment, are usually sufficient to produce the desired effects.

### PAINT AND FILM PROPERTIES

It has been common practice to divide interior finishes into four major classifications based on the surface characteristics of the dry films. These groupings consist of flat paints, semi-gloss paints, gloss paints, and enamels. The essential differences between these types may best be explained by taking into consideration some fundamental precepts.

**Binder Influence.** The relationship of binder to pigment by volume is of paramount importance because of its predominating influence on the physical and optical properties of any given pigmented system. The general nature of the finish desired in the ultimate film dictates, within reasonable limits, the ratio that must be used. Inherent oil

requirements of the pigments involved, specific film characteristics, and attributes of the vehicle in question constitute other influential factors which have a direct bearing on the amount of binder to be used per unit of pigment volume.

It is desirable to express the ratio of pigment-to-binder (or vice versa) on a volume basis as this represents a more accurate means of

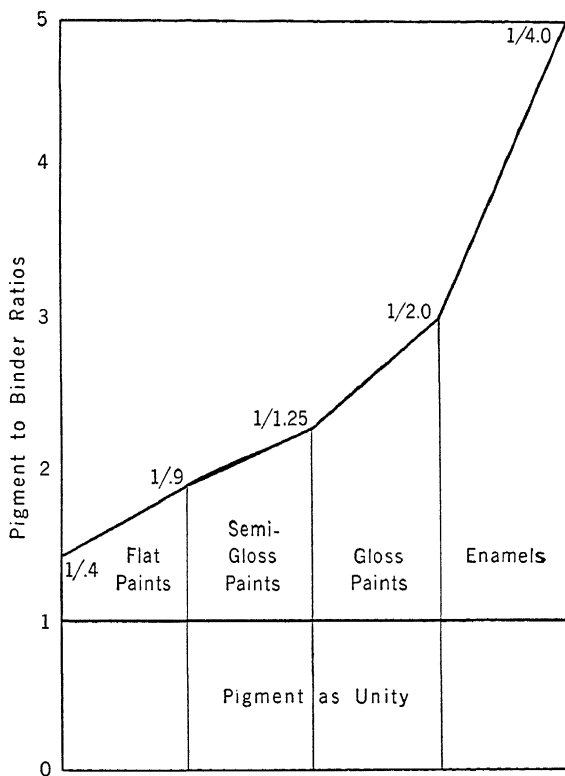


FIG. 1. Pigment to Binder Relationships by Volume.

expressing the true relationship that exists between these two components of the dried film. Obviously, the ratio of binder to pigment is subject to variation for each group of paints and is, as well, a variable within the respective groups as depicted graphically in Fig. 1. The pigment concentration is necessarily limited for each type of product. For example, in flat paints it may fall anywhere within the range of 71.5 to 52.5 per cent ( $P/B = 1/4$  to  $1/9$ ) by volume based on total solids. Semi-gloss and gloss paints generally fall within the range of

52.5 to 33 per cent ( $P/B = 1/9$  to  $1/20$ ). Enamels may vary from 35 to 20 per cent ( $P/B = 1/20$  to  $1/40$ ).

Obviously these limits are not closely defined and furthermore there is no sharp line of demarcation between adjacent groups. To repeat, the ratio of binder to pigment by volume is subject to variation, depending upon the major formula components, and is governed by the specific system in question. In general, as the pigmentation is increased, the gloss decreases proportionately and, as a result, the amount of binder used per given unit of pigment is determined by the film surface effects desired. Other film properties which are discussed later are also influenced by these ratios.

**Suspension.** A certain amount of pigment separation and settling occurs in all paints and enamels, the nature of which differs for the different types of systems. In many cases slight separation, leaving a relatively thin layer of supernatant liquid on the surface, is desirable as a safeguard against skinning in the container. The settled portion of the pigment in such a case exists usually in the form of a soft, mushy cake which can readily be reincorporated.

Settling becomes objectionable when the settled pigment layer exists as a dry, tough, and compact cake which cannot be reincorporated into the vehicle with ease.

Croll (4) discusses settling with particular reference to the effect of particle size, mechanical dispersion, degree of wetting, shape of the pigment particle, and viscosity of the vehicle. The "settling force" is defined as the weight of a unit volume of pigment minus the weight of an equal volume of vehicle. It is claimed that, when a pigment is immersed in a liquid, certain forces are exerted between the pigment and the liquid and between various particles of the pigment, the magnitude of which is proportional to the area of surface of pigment-liquid interface. Decreasing the pigment particle size increases the total surface area, which also increases the internal forces.

Croll also advocates perfect mechanical dispersion of a pigment in a paint liquid. In cases of enamels, conditions of viscosity and yield value of the vehicle and extremely fine particle size (large surface area) of the pigment must be depended upon to oppose the settling forces. Less thorough wetting between pigment and vehicle is often accompanied by flocculation resulting in loosely held groups of pigment particles which usually prevent hard, dry caking of the pigment.

Small individual particles, thoroughly wetted, may eventually settle to the bottom of the container if no flocculation or structure formation occurs to restrain this movement. McMillen and Glaser (11) suggest

utilizing the tendency of pigment vehicle mixtures to become plastic as a means of preventing settling. The strength (rigidity or yield value) of the plastic (paint) may be made sufficient to arrest the movement of the particle under the influence of gravity.

Settling may be overcome by establishing a rigidity in the paint which will support the net weight of the pigment structure. Practically, this may be attained through various means such as finer particle size, high viscosity of the vehicle, gel structure within the system, and flocculation of the pigment. Gel-forming substances such as the stearates invariably prove beneficial not only in improving suspension but also frequently in overcoming settling difficulties entirely. The incorporation of small amounts of water (1 per cent by volume), usually added in the form of soap solution, serves as a reliable means of promoting good suspension. The efficiency of water depends on the degree of flocculation attained, which in turn is governed in part by the dispersing tendencies of the vehicle. This holds true especially for products other than gloss paints and enamels. Caution must be used in gloss paint systems as water may have a deleterious effect on gloss.

Whenever any appreciable quantity of reaction products is formed in a system the effects will vary according to their solubility. The insoluble products tend to set up a gel structure which will aid suspension, whereas any soluble reaction products formed may actually exert a dispersing influence having an adverse effect on settling.

Settling tests are very time-consuming in view of the fact that six months to a year of shelf storage is required under natural conditions before any conclusions can be drawn. In order to overcome this, various accelerated settling tests have been devised (5, 27, 28), which have been based upon heat, dilution, centrifugal force, and various combinations of these factors, to hasten settling. Various procedures must be used for different types of products. These tests are not entirely satisfactory because conditions not encountered in normal paint aging are produced, and the forces involved are sometimes more severe than the force of gravity. McMillen and Glaser (12) suggest measuring the variation in rigidity with increasing pigment content as a means of predicting the severity of settling to be expected. In any event such accelerated tests as have been proposed serve to give indications only, and actual shelf aging is still considered the most reliable method.

A numerical system for grading the caking of pigments in paints has been found convenient and practical, and the following method is

therefore suggested concerning standards and designations which may be used in recording degree of caking, type of sediment, and type of dispersion in the supernatant liquid. All gradings have a similar range with a convenient and easily comparable scheme for recording and interpretation of data. Numerical evaluation is particularly desirable because of its applicability and significance in making intermediate gradings in a series of samples.

*Degree of Caking.* "Degree of caking" has reference to the *extent of hard caking*.

Grading is done with a regulation 6-inch tapered spatula and is applied particularly to the pigment cake in a quarter pint can.

C 10+ Perfect dispersion—no sedimentation whatever apparent.

C 10 Gives practically no resistance to spatula. No deposit brought up with spatula—however, pigment may be rather well settled out.

C 9 Well-defined but very soft cake offering a slight but definite resistance to sideways motion of spatula (flat side of spatula foremost).

C 8 Spatula readily drops through to bottom of can under its own weight. Cake has toughened slightly so that portions can be removed with spatula.

C 7 Just possible to move spatula through cake sideways. Slight but definite edgewise resistance to spatula. This is the important point of initial failure by caking, i.e., where caking begins to become truly objectionable.

C 7— Practically impossible to move spatula sideways through cake.

C 6 Well-defined resistance to spatula when moved edgewise with one hand.

C 5 Just possible to move spatula edgewise with one hand.

C 4 Necessary to use both hands to produce edgewise motion of spatula.

C 3 Barely possible to move spatula edgewise through cake.

C 2 Impossible to move spatula edgewise when once inserted in cake.

*Type of Sediment.* "Type of sediment" has reference more particularly to the nature of the cake and describes its condition in a manner supplementary to the following mentioned grading. Admittedly divisions in grading are somewhat arbitrary.

- T 10 Mushy and very loose cake.
- T 8 Soft and gummy.
- T 6 Noticeably tough and gummy.
- T 4 Dry and tough cake.
- T 2 Dry and brittle cake.

*Dispersion in Supernatant Vehicle.* "Type of dispersion" describes the condition of the supernatant vehicle with regard to the amount of pigment still dispersed.

- D 10+ Perfectly dispersed.
- D 7 Very cloudy.
- D 5 Cloudy below but clear on top.
- D 2 Completely settled out, leaving a clear vehicle free from dispersed pigment.

In addition, the depth of cake may be indicated in percentage. This can be conveniently measured with a spatula having a suitable scale marked on the blade. The ratio of the depth of cake to the depth of the paint can thus be conveniently estimated and recorded. Such measurements may be indicated by "H" followed by the numerical value.

For example, a paint sample found to have a well-defined but very soft cake offering a slight but definite resistance to sideways motion of the spatula, being soft but possibly just a trifle gummy, with a layer of clear vehicle over a cloudy layer above the cake and a cake depth of 20 per cent, would be designated in the following manner: C9-T8-D5-H20. The first grading is usually the most significant.

**Consistency.** Consistency is an important paint property in view of its influence on other properties such as suspension, ease of brushing, leveling, and hiding power. The first three properties in all normal pigmented systems are usually affected in a manner inversely proportional to the consistency or body of the system. This holds true especially if the increase in consistency is caused primarily by flocculation of the system.

According to Smith (22) the consistency of a paint is affected by four sets of factors: (a) the viscosity of the liquid components, (b) the weight, volume, and particle properties of the solid components, (c) the manner in which the components have been admixed and the mechanical forces that have been employed, and (d) temperature, the effect of which will be greater the more viscous the liquid components and the higher the proportion in which they are present.

Although factors such as these should not be overlooked, flocculation of the system is also a very important factor in causing high apparent consistency. The extent of flocculation of pigmented systems frequently has a direct bearing on both degree and type of con-

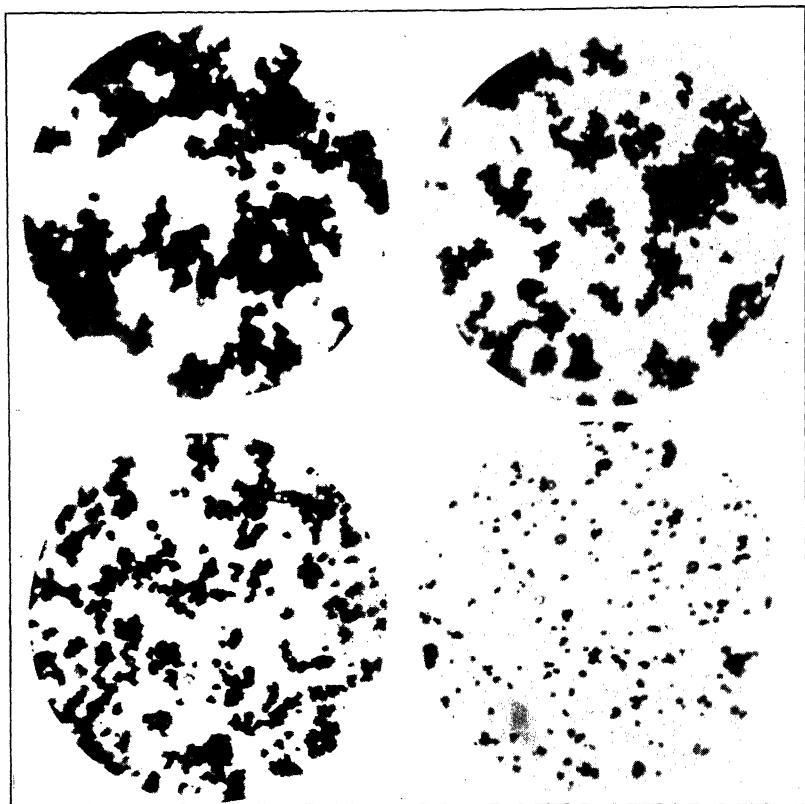


FIG. 2. Differences in Degree of Flocculation.

sistency obtained in such compositions. The systems may differ considerably in apparent viscosity because of differences in their flocculated structure. If pigment particles are deflocculated (highly dispersed) in the vehicle, the system will tend to behave more nearly as a true fluid, shearing force being strictly proportional to rate of shear (16). With a flocculated structure, however, the apparent viscosity (especially at low shearing forces) will be higher. A higher shearing force is necessary to furnish a given rate of shear because a part of

the force is required to overcome the flocculation forces between pigment particles.

Differences in degree of flocculation and differences in resultant pigment structure are demonstrated by photomicrographs in Fig. 2 (16). The various stages of flocculation ranging from a deflocculated system to one that is highly flocculated are readily apparent.

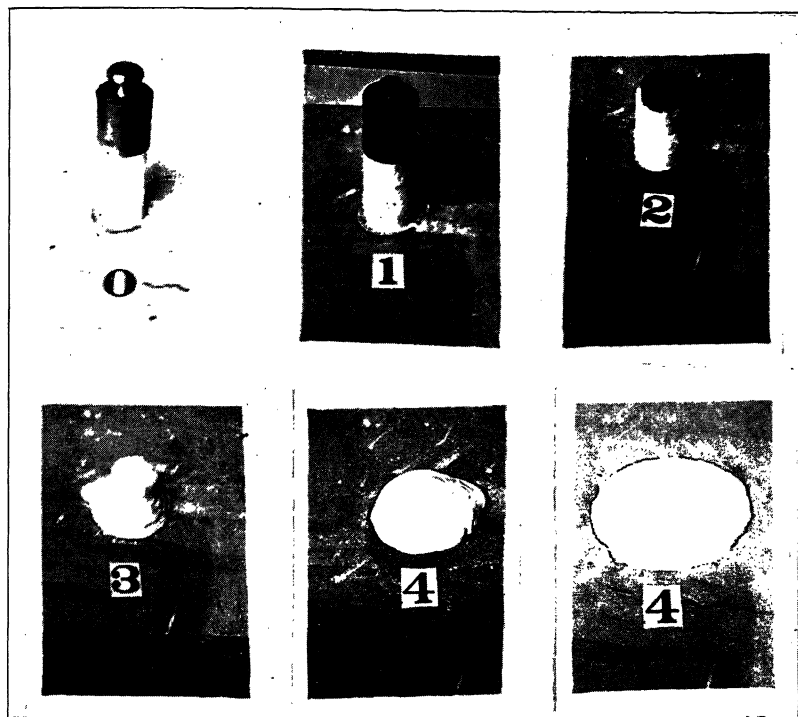


Fig. 3. Influence of Flocculation on Consistency.

The effect of these differences in flocculation on consistency is demonstrated in Fig. 3 (16), which shows lithopone-mineral spirits systems treated with polar agents. Here the influence of flocculation on consistency is quite obvious. Furthermore, this demonstrates a direct relationship between consistency as influenced by flocculation and flowing characteristics.

From a practical standpoint, the methods most frequently employed to attain the desired consistency depend either on flocculation of the system or reaction by virtue of soap formation or a combination of



both (26). Flocculation of the pigment may be induced by utilizing a relatively poor wetting vehicle system, or by the addition of water, or both. Small amounts of water (approximately 1 per cent by volume) usually added in the form of a mild soap solution may be used to obtain the desired results. The degree of body obtained when water is used is a function of the hydrophilic nature of the pigments used, supplemented by certain vehicle characteristics. Pigments inherently sensitive to water will show a very decided tendency to flocculate in relatively poor wetting systems, whereas in good wetting media the systems will be far less susceptible to flocculating tendencies.

Livering involves a vehicle thickening effect rather than a pigment flocculation effect, and it affects consistency significantly. Pigments are often responsible for the thickening, owing either to formation of viscous soaps or to removal of dispersing agents necessary to keep the vehicle components compatible with each other. According to the Chicago Paint and Varnish Production Club (3) livering or gelling of paint liquids is due to the presence of gel-forming components such as highly polymerized oils or soaps. The former may be peptized by means of added organic acids. Proper cooking procedure and proper selection of pigments are suggested as a means of control. Reduction of vehicle acidity and the use of large particle size zinc oxide are advocated.

Increased consistency due to livering is usually undesirable because of package instability. Furthermore, livered paints always present application problems in that they pull under the brush and may have a tendency to sag.

False body in such paint systems as discussed differs from thixotropy in that the former depends upon the state of dispersion of the pigment, whereas the latter depends upon the reactivity of the components. According to J. Pryce-Jones (19) thixotropy in paints is subject to four factors: concentration of the pigment, degree of wetting of the pigment, the presence of soap, and the presence of water. McMillen (13) made measurements of thixotropic changes in paint to show that good leveling is obtained if the thixotropic rate of plasticity regained after application is fast enough to overcome the tendency to sag but slow enough to allow elimination of brushmarks before the paint sets. Gamble (5) has shown correlation between such properties as pigment settling tendencies, brushability, and leveling with the thixotropic characteristics of a paint.

The results of tests conducted by Kewish and Wilcock (8) led to the conclusions that thixotropy increases with increasing pigment con-

centration, some sort of critical point occurring at 30 per cent pigment by volume; that it increases with increasing aluminum stearate content; that it is not a simple function of the viscosity of the oil; that untreated oils yield paints with higher degrees of thixotropy than do bodied oils; and that the initial effect of blowing oil is to increase thixotropy and that a decrease in thixotropy is not observed until after prolonged blowing. The effect of these variations on leveling is almost the exact reverse. Deviations from this relationship are a result of the fact that initial leveling is a function of the maximum fluidity of the paint, whereas subsequent leveling depends upon the change of fluidity with time.

In view of the numerous influential factors involved it is definitely impossible to predict consistencies of paints from oil absorption data. Sward and Hart (25) have determined that the order of consistency of paints made with various pigments and one liquid is not necessarily the same as with other liquids. Their attempts to evaluate separately the influences of pigment and vehicle upon consistency were unsuccessful.

Of the numerous methods available for measuring consistency of pigmented paint systems, the Krebs modified stormer method, the details of which are described in Chapter 10A, has been found very successful. The instrument is simple, dependable, and permits rapid determinations. At the same time it predicts inherent consistency within a reasonable degree of accuracy for the majority of paint bodies. It does not measure degree of thixotropy nor is it applicable to extremely heavy paints which are inclined to be short and choppy because the forked paddle creates furrows, thereby yielding a fictitious shear rating. A new type of submerged paddle has been proposed to overcome this fault.

Wicker and Geddes (29) have proposed a new recording viscometer which combines the principles of the modified stormer and the McMichael instrument. A cylindrical container is rotated at constant speed, the liquid within imparting torque to a paddle connected with a spring. A lever arm records the consistency upon a moving chart.

Unlike the stormer, the recording viscometer can be used to obtain a continuous record of consistency. It is possible not only to measure thixotropic and rheoplectic paints but also to follow the thickening of water-sensitive systems, effect of bodying agents, and similar phenomena of interest to the paint chemist.

**Brushing.** A pigmented system is normally considered as having good brushing properties when it shows a minimum resistance to

spreading under the brush. In other words, it must be free from excessive drag or pull and lend itself to uniform distribution over the surface with a minimum number of brush strokes. At the same time, it should have sufficient build to produce a cushion effect under the brush.

Spreading rate and lap time are closely associated with brushing characteristics. The spreading rate of paints varies in a manner inversely proportional to the pull under the brush. Hard brushing paints will yield low spreading rates, whereas easy brushing paints will yield relatively high spreading rates. Actually paints may offer such little resistance as to be objectionable because of high spreading rate and correspondingly lower hiding power.

Lap time is governed largely by the initial boiling point and distillation range of the solvents used as well as the solvent retention properties of the vehicle solids and their state of fluidity after partial evaporation of the thinner. Highly viscous gels will offer maximum resistance to brushing under these conditions.

Flocculation of a system definitely contributes to ease of brushing. Paradoxically, brushing is affected in a manner opposite to that of brushmark elimination. Thus a flocculated system will brush out more readily than will a deflocculated one. Forces used in brushing are in the order of magnitude of those used in consistency measurements. If a pair of paints, one flocculated and the other deflocculated, are adjusted with thinner to the same apparent viscosity at low shearing forces (same flow), the deflocculated system will have the higher apparent viscosity at the higher shearing force used in brushing (higher body). The flocculated system loses part of its apparent viscosity where the brush is used vigorously, whereas the deflocculated system does not.

The measurement of brushability has been largely on an empirical basis. Several devices have been suggested for measuring this property. Among them is a machine by Baldwin and Gardner (2) which consists of a freely rotating drum arrangement driven by a circular brush, and the results are expressed on an arbitrary scale.

**Leveling.** Flow and leveling characteristics of paint systems are definitely influenced by the state of pigment structure. Highly flocculated systems have a tendency to retard flow and leveling properties, whereas deflocculated systems will flow more freely. Thus, the degree of wetting and the dispersion attained in a given system have a direct bearing on this property. \*

It must be recognized that flow adjustment is a compromise. Whereas good flow is desirable for the elimination of brushmarks, reduced flow is necessary for prevention of sagging on vertical surfaces. It is therefore essential that the state of dispersion be controlled to yield the desired properties.

A poorly wetted pigment in a given system will show poor leveling properties, whereas a well-wetted system usually possesses good leveling characteristics. Furthermore a highly dispersed system (devoid of pigment structure) usually shows definite sagging tendencies. In other words, a system may be well wetted and yet not have any sagging tendencies. However, when excellent wetting and a high degree of dispersion are combined there usually is a definite sagging tendency.

Similarly these properties are affected by the alkaline potential of a system. Free alkali reacts with the acidic constituents of the vehicle to form soaps which may be of the soluble or insoluble type, depending upon the nature of the reactive compounds. Negative alkaline potential results in poor wetting, yielding a highly flocculated structure deficient in flow characteristics. Conversely, a positive potential gives good wetting which reduces the degree of flocculation and produces satisfactory flow. In the event that the alkali potential is excessive, exceptionally good wetting will result, with little or no flocculation and correspondingly increased flow.

Poor leveling may also result because of too rapid drying of the film, in which case the factors responsible will have to be removed or corrected.

**Hiding Power.** The opacity or hiding power of a paint is a measure of the ability of the paint to obscure the surface over which it is applied, and it is frequently expressed in terms of the particular area which can be hidden by a definite volume of the paint. Pigments differ enormously in their hiding power characteristics and consequently also differ in their ability to impart hiding power to a given paint system.

Hanstock (7) showed that the light transmitted directly through films made from any one paint decreases logarithmically with increasing film thickness whereas the amount of light diffusely transmitted decreases much less rapidly. Hanstock treats the relationships between the thickness and opacity of a paint film and its ability to hide varying degrees of contrast mathematically. He also shows that the wet film hiding power of white paints is largely determined by the reflecting power of the surfaces of the pigment particles. This reflecting power, in turn, is largely determined by the values of  $n$  (re-

fractive index) for pigment and vehicle in the usual paint film. If, however, the film of vehicle on the surface of the pigment particles is very thin, the effect of the vehicle on reflecting power of the pigment particles may be considerably reduced and the pigment particles may retain more of their reflecting power than usual. This effect is important in connection with change in brightness during paint drying. Composite pigments frequently possess optical properties different from those anticipated from their components.

Considering paint as a concentrated suspension of pigment particles in a binding medium it may be assumed that the hiding power of the system is derived from light reflection or absorption at the surfaces of these pigment particles. Pigments differ in their relative abilities to reflect light and in consequence, at equal formulation, paints containing high strength pigments will reflect more light in thin layers and have higher hiding powers. With a given pigment, increased concentration also tends to increase the hiding power of the paint.

The effect on hiding power of changing pigment concentration in a paint cannot always be predicted. Since the paint is a concentrated system, pigment particles tend to be close together and to interfere with one another. As the concentration of pigment in the paint is increased, more interference is brought about and each unit of pigment becomes less effective. The general effect of increasing pigment concentration is to raise the hiding power of the paint but by an amount not in proportion to the pigment increase. In some cases, the loss in pigment efficiency due to increased concentration may more than offset the gain in total hiding power brought about by increasing the amount of pigment.

The hiding power value of a given pigment is subject to extreme variation, depending upon the way in which it is used. According to Sawyer (21) it is impossible to assign to any given pigment an absolute hiding power value having much meaning, since it is easily possible to vary the hiding power value of a single pigment as much as 100 per cent simply by varying the paint composition in which it is used. An absolute pigment hiding power therefore has no meaning except under conditions of use very closely approximating the conditions used in testing. Furthermore tables of hiding power relations between pigments also are useful only for conditions of use approximating the conditions of test.

As already pointed out, increasing the pigment concentration in the film decreases the efficiency of the individual particle in the film. This decreased efficiency is reflected in decreased pigment hiding power.

If, however, concentration of pigment in the film is increased sufficiently, the pigment efficiency increases. Because insufficient vehicle is available to cover all the pigment, the surface of the paint becomes microscopically rough, and an increased amount of light is reflected from the surface of the film.

In the range of enamels and semi-gloss paints, pigment efficiency (and pigment hiding power) vary inversely with pigment concentration. Increasing pigment concentration decreases pigment efficiency and causes a smaller increase in paint hiding power than would be expected, whereas decreasing pigment concentration improves pigment efficiency and causes less decrease in paint hiding power than would be expected.

In considering the relation of one pigment to another it is necessary to consider not only the relative hiding powers of the two pigments but also the relative hiding powers of the paint compositions in which the two pigments are compared. Whether a pigment has two, five, or ten times the hiding power is a matter of no account unless essentially the same painting composition can be made from either one.

Lightbody and Dawson (11) have found that modern binders for architectural enamels and industrial baking enamels, when utilized in practical compositions, cause large differences in hiding powers. A large part of these differences has been ascribed to the necessity of using the short oil binders at low non-volatile contents due to the high viscosity of the binder solids and the necessity of preparing paints in a low, practical consistency range. Consequently, equal volumes of paint result, with the short oil, high-binder-viscosity liquids, in thinner films, greater pigment crowding, and less efficient utilization of the pigment.

Even at equal pigment volumes in the film, however, differences in hiding power of about 20 per cent exist between vehicles. These differences are not due to binder refractive index, binder color (although binder color can cause differences of the same magnitude), or to the solvent.

Lightbody and Dawson attribute these differences to differences in degree of deflocculation of the pigment.

It is also a recognized fact that wet film hiding power may differ enormously from dry film hiding power. This holds true especially for flat paints or in general for paints of relatively high pigment concentration. Other factors, the most prominent of which is film thickness, also have a direct influence on hiding power. According to McMullen (14) there is an optimum pigment-volume ratio and film thick-

ness at which the maximum hiding power of a pigment is obtained and in all probability this optimum condition varies for each pigment. McMullen assumes that light falling upon any surface divides itself into three parts—reflected, absorbed, and transmitted—and that reflectivity and transmissivity values are closely related to hiding power. It is clearly shown that these values are greatly influenced by pigment thickness, actual film thickness, and pigment volume ratio. It is also pointed out that for certain lower film thicknesses there is an optimum pigment volume ratio at which the maximum light-reflecting power of a pigment may be obtained for commercial application. The actual measurement of hiding power introduces further complications because of the lack of a universally accepted method which can be used to express the results with practical significance. According to Stutz and Haslam (24) indirect measurements of hiding power arrived at by measuring related properties such as tinting strength are not satisfactory. They also point out that the paint-out test is correct in principle but is time-consuming in application. It is claimed that the Pfund cryptometer measures hiding power simply and accurately but is applicable only to wet paints and to paints of over 70 per cent brightness. The Pfund black-and-white cryptometer gives an accurate measure of the wet hiding power of a paint of any brightness. The Haslam spinning-film method measures hiding power accurately but requires expensive apparatus. The modified paint-out test of Gardner is less accurate but simple and inexpensive.

Ayers and Clewell (1) suggest a simple brightness photometer to determine: (a) hiding power of paints, (b) discoloration or differences in hue of white inert or opaque pigments, and (c) tinting strength of black or colored pigments used with white pigments. It is claimed that in the visual comparison of two whites the instrument can detect a difference of 0.1 per cent.

McMullen (14) suggests the spectrophotometer as a means of determining hiding power of pigments accurately, based on light-reflecting power.

**Color.** Color and color permanency of paint systems are influenced by type of pigment used, concentration of the pigment, and vehicle characteristics. A measure of brightness is usually considered as a good indication of color and may be used to denote color differences. Generally speaking, in low sheen products, brightness usually varies in a manner directly proportional to pigment concentration. Pigments show maximum reflection values at high pigment concentration. Con-

versely at lower concentrations these same systems will show a corresponding decrease in brightness.

The Philadelphia Paint and Varnish Production Club (17) found that color change may be due to one or more of a number of several different causes among which are (a) photochemical changes caused by actinic light, (b) changes in the exposed surface of the film, (c) changes in the relative indices of the film components, and (d) chemical reactions resulting in changes in composition of colored pigment constituents.

### Flat Paints—Properties

Flat paints, as the name signifies, are designed so as to produce relatively low angular sheen in the dried film. There are no restrictions concerning pigment and vehicle components other than the limitations imposed by the performance requirements desired in the finished product. This affords a wide leeway in the selection of ingredients; however, in the actual compounding, certain characteristics and influential factors should be taken into consideration.

Of particular importance in the formulation of flat wall paints is the ratio of pigment to binder content. The amount of total binder per given volume of pigment present in a formula exerts a very definite influence on such properties as sheen, color, hiding power, enamel hold-out, and washability, and is governed in part by the inherent oil absorption of the pigments used. Obviously, then, the pigment-to-binder ratio becomes a variable depending upon the types of pigments involved and the film properties desired in the finished paint.

The pigments of high oil absorption require more binder to satisfy their requirements than the pigments of low oil absorption in order to obtain corresponding film properties. At the same time, extenders are not without influence. Soft and easy-wetting extenders, such as whitening, require less binder than the siliceous and silicate types to yield comparable film properties.

**Consistency.** There are a number of different methods available for producing varying degrees and types of body. The consistency of a flat paint for instance may be increased (a) by the selection of high oil absorption prime pigments and extenders, (b) by increasing the vehicle solids or increasing the viscosity of the oils used, (c) by increasing total pigment concentration, (d) by incorporating stearates, (e) through chemical reaction, and (f) by the addition of various bodying agents.



The addition of small amounts of water is frequently resorted to as a simple yet generally effective means of controlling consistency. The effect will be influenced by the hydrophilic nature of the pigments used and by vehicle acidity. Ordinarily oleoresinous systems of a highly acidic nature, especially in the presence of relatively poor wetting oils, may yield excessive body accompanied by lack of flow. Neutral vehicles usually lack the desired wetting action, while vehicles of excessive acidity may cause an extensive puffing action upon water additions, especially if the pigments used show affinity for water.

The type of organic acids present may also influence the degree and type of consistency obtained. The effect of some of the more common organic acids is shown in Table III.

TABLE III  
CONSISTENCY AS AFFECTED BY ORGANIC ACIDS

	Control	Tung Oil Acids	Stearic Acid	Naphthenic Acid	Linseed Acids	Perilla Acids	Soya Acids	Rosin Acids
Consistency (No water)	83	78	78	76	74	74	75	82
Consistency (1% water)	122	123	142	132	132	132	134	140
Puff condition (with water)	None	Def.	V. Def.	V. Slight	Def.	Def.	Def.	V. Def.

The consistency is expressed in modified Stormer units and the puffy nature is based on an arbitrary grading. From these data it is apparent that all the acids except naphthenic caused a definite increase in rigidity, with the stearic and rosin acids outstandingly effective. One interesting observation is that in the tung oil acids the actual consistency did not exceed that of the control paint; nevertheless definitely more puff was in evidence. Conversely, the paint containing naphthenic acid was heavier in consistency but only very slightly more puffy than the control paint.

Further evidence indicates that the presence of excessive amounts of rosin acids may cause abnormal bodying effects. The data in Table IV show the effect produced by the addition of rosin acids to a paint system, in the form of a limed-rosin gloss oil.

TABLE IV  
CONSISTENCY AS AFFECTED BY LIMED ROSIN

	16% of Veh. Solids as Limed Rosin		8% of Veh. Solids as Limed Rosin		No Limed Rosin	
	No Water	1% Water	No Water	1% Water	No Water	1% Water
Imm. cons.	84	140	89	134	85	92
1 wk. cons.	90	140	89	134	91	108
8 mos. "	89	141	88	113	100	112
16 " "	84	139	95	102	95	105

The effect of the higher percentage of rosin acids is manifested by the marked increase in consistency in the presence of water, whereas, in the paint containing no gloss oil, only slight thickening took place and the body remained relatively constant. In the intermediate paint, initial thickening took place followed by after thinning, thus showing the effect of reaction in the system.

Consistency effects may also be influenced by extenders. For instance, the magnesium silicate and diatomaceous earth types yield increased body as compared with the calcium carbonate materials. Furthermore, the effects obtained from a single group of extenders may vary significantly. Calcium carbonate, for example, an extender used rather widely in flat formulations, varies appreciably in oil absorption and alkalinity. The alkali present, being of the soluble type, reacts readily with the free fatty acids of the vehicle to form soaps. The nature of these soaps may vary and consequently may affect the results obtained. Some reaction products may serve as dispersing agents, thereby breaking the existing gel structure and producing thinner consistency. Others, especially the insoluble types, may contribute to the structure of the system and cause a further increase in consistency.

The presence of non-siccative metallic soaps leads to increased consistency by virtue of the gel-forming tendencies of these products. The resultant increase will vary, depending upon inherent properties of the soaps used, mill conditions, etc. For instance, grinding at elevated temperatures promotes efficiency of gel formation with correspondingly greater increase in consistency.

**Suspension.** Assuming that the pigments in a given paint system are well wetted and dispersed, the addition of agents such as aluminum stearate, zinc stearate, or any other material which tends to build up a supporting pigment structure in the system, will further improve suspension. The addition of water serves the same purpose, usually attained through flocculation.

Prime pigments and extenders differ in their ability to remain in suspension. Some of the pigments of higher density are more prone to settle than the low-density, high-bulking pigments. For example, titanium calcium pigments show less tendency to settle than the barium base pigments.

Some of the prime pigments have been surface-treated with an organic coating which greatly improves the suspension properties of the pigment. This same generalization applies to the extenders. Calcium carbonate types suspend better than the barium sulfate types. At the same time the magnesium silicates and diatomaceous silicas are generally superior to the calcium carbonates.

Vehicles are not without influence in that they differ significantly in their effect on suspension of finished paint. They are rather difficult to classify because of so many variable factors; however, as a group, the phenolic types are worse in this respect than the non-phenolic vehicles.

Suspension is also related to consistency. Thin-bodied paints in a given system are more prone to settle than the same paints at heavier consistency. Furthermore, suspension is a function of the percentage of vehicle solids in a given paint system. A vehicle should contain not less than 30 per cent solids by weight based on the total vehicle. Frequently higher solids are employed as a factor of safety.

**Hiding Power.** In speaking of hiding power, reference is usually made to dry film hiding; however, in many instances, the wet film hiding is equally important. Flat paints having high dry film hiding have significantly lower wet film hiding power. Both wet and dry film hiding power will vary appreciably, depending upon the pigments used and the paint composition involved.

The hiding power value of any given pigment is subject to extreme variation, depending upon the paint composition in which it is used. The high oil absorption (high consistency) pigments offer distinct advantages in hiding power at the low binder contents at the expense of film properties. This hiding power advantage, however, is minimized at the higher binder contents. The lithopone pigments decrease in

hiding power somewhat more rapidly than the calcium base titanium pigments as the binder per unit volume of pigment is increased.

Incomplete dry film hiding power relationships that may exist between prime pigments are demonstrated in Figure 4. The only difference existing between the three paint systems *A*, *B*, and *C* is in

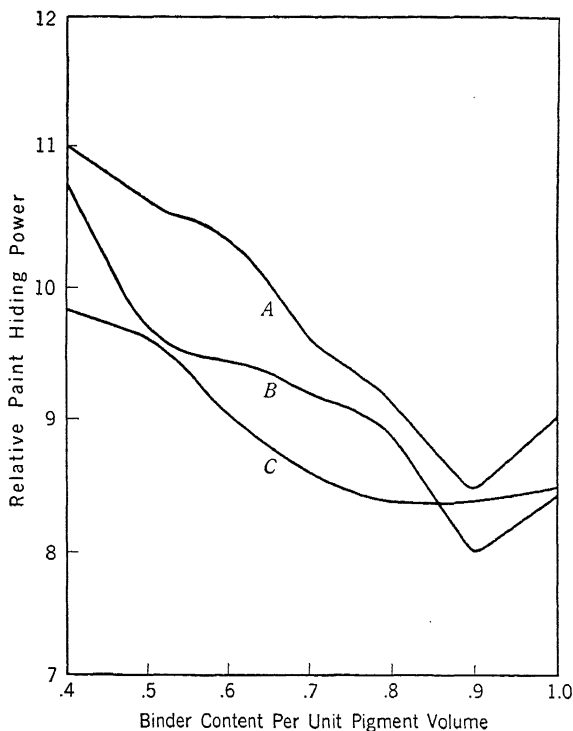


FIG. 4. Relative Paint Hiding Power.

the type of prime pigment used. The curves presented are based on a relative comparison made under carefully controlled conditions; however, they cannot be regarded as absolute. They not only show differences in relative hiding power values of the different pigments used, but also demonstrate the significant decrease in hiding power for each system as the binder content per unit volume of pigment is increased. The general trend indicated by these curves represents the general behavior of flat paint systems as conditions are changed.

It has been recognized that other factors, the most prominent of which is film thickness, also have a direct bearing on hiding power.

Figure 5 shows the hiding power results obtained from these same paint systems applied at increased wet film thickness. It is of interest to note that the dry films in this case are 30 per cent greater in thickness than those in Figure 4 and that the increase in dry film incomplete hiding power is not directly proportional to the increased film

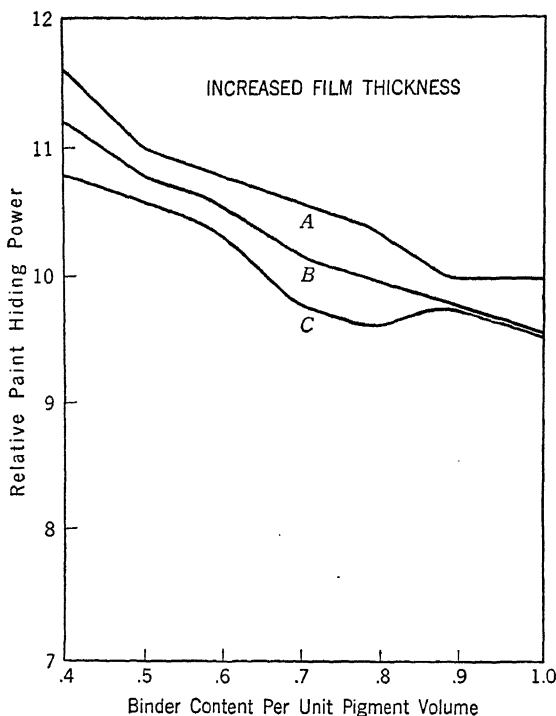


FIG. 5. Relative Paint Hiding Power.

thickness. The hiding power relationship of the three prime pigments is generally the same as shown in Figure 4. These graphs exhibit the same trend toward decreased hiding power as the binder content is increased. It is also apparent that the greater film thickness has minimized differences in relative hiding power and has favored the lower hiding systems. This emphasizes the necessity of controlling spreading rates when hiding power comparisons are made.

According to Rhodes and Starr (19), the addition of small quantities of carbon black or Prussian blue definitely increases the hiding power while decreasing brightness only slightly. Larger amounts of colored pigments have a more pronounced effect. It was also found that

with very small quantities of Prussian blue the ratio of the increase in hiding power to the decrease in brightness is greater than with carbon black. The addition of aluminum powder greatly increases the hiding power but lowers the brightness and causes the dry film to have a flecked appearance. Rhodes and Starr suggest as advantageous the use of aluminum powder in undercoats for white finishing coats.

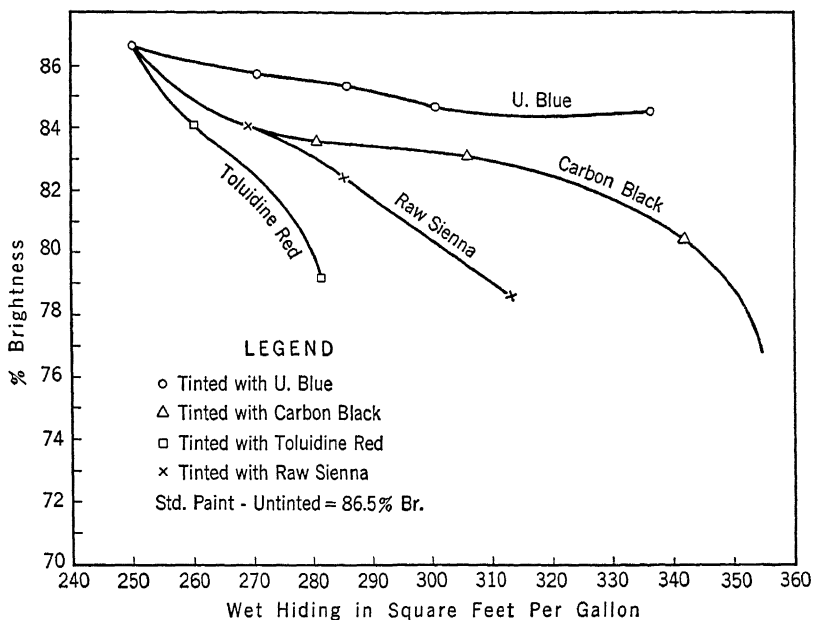


FIG. 6.

Other investigations (9) have shown that both wet and dry film hiding power may be increased significantly through the use of small quantities of tinting agents accompanied by a relatively small drop in brightness. Furthermore, these results indicate that different tinting agents will show marked differences in their effect on brightness per unit hiding power. Figure 6 demonstrates graphically the effect various colored pigments have on the ratio of increased wet hiding power to the decrease in brightness. Figure 7 demonstrates the ratio of dry film hiding power to the decreased brightness. It is readily apparent that ultramarine blue is the most efficient of the four tinting colors tested. It may be observed that the addition of ultramarine blue showed an average increase of 14 per cent and 10 per cent in

wet film and dry film hiding power respectively for 1 per cent decrease in dry film brightness.

**Color.** The color and brightness of flat paints are influenced by (a) prime pigment, (b) extender, (c) prime pigment-to-extender ratio, (d) pigment concentration, and (e) inherent color of the vehicle used.

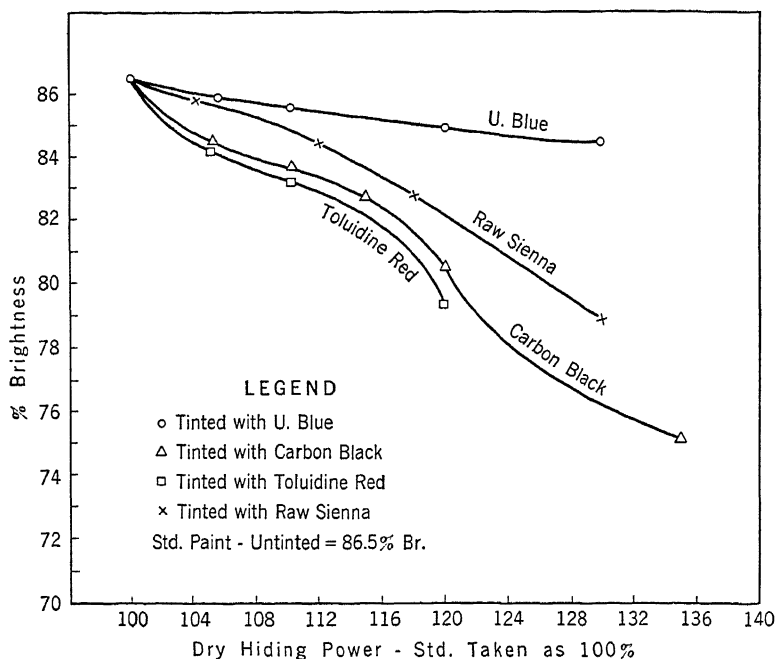


FIG. 7.

In general the extended titanium pigments yield paints of better color and brightness than the lithopone types. Maximum brightness is obtained at low binder contents for both the lithopone and titanium pigments, especially those types having high oil demands. Brightness varies in a manner inversely proportional to the binder content per unit volume of pigment. At high pigment concentration exceptionally good color and brightness are obtained with corresponding decrease in these properties as the binder is increased.

The effect of extenders on this property varies in a manner directly proportional to the amount used. Further variations will be experienced depending upon the type; however, with all normal types of extenders, as the amount is increased the color drops correspondingly.

Some extenders are deficient in inherent color and consequently have rather pronounced effects on the color of the paint. Others are highly abrasive and discolor the paint during the grinding operation.

**Sheen.** Sheen (angular reflectivity) may be controlled (*a*) by manipulating the pigment-to-binder ratio, (*b*) by selection of low sheen pigments or extenders or both, and (*c*) through the use of various flattening agents.

High pigment concentrations produce low sheen. As the binder is increased the resultant sheen will also increase. Extremely fine prime pigments (primarily intended for gloss paints and enamels) will yield higher sheen than the coarser particle types. This also holds true for the extenders. Inert pigments such as the magnesium silicates and silica are more efficient for flattening purposes than the calcium carbonate type extenders. The diatomaceous earths are even more effective in lowering the sheen.

The addition of soaps such as aluminum stearate, zinc stearate, calcium stearate, and zinc palmitate also contributes to lower sheen, the effect being directly proportional to the amount added.

Reducing the binder content beyond the low limits which are normally required to yield satisfactory film properties is the least desirable method for sheen control.

**Brushing.** Ease of brushing may best be accomplished through (*a*) vehicle manipulation, (*b*) consistency control, and (*c*) introducing pigment flocculation.

Ease of brushing will vary in a manner inversely proportional to the inherent viscosity of the oils and varnishes used. Furthermore short-oil varnishes will result in greater brushing difficulties than the long-oil products. The use of heavy-bodied oils produces hard brushing. The one exception to this is bodied fish oil which shows this tendency to a much less degree than the other oils which are normally used. Frequently a vehicle compromise consisting of a satisfactory blend of bodied and unbodied oils may be necessary to produce the desired results.

Brushing will also vary inversely with the percentage of vehicle solids. High solids may show decided pull under the brush. This may be further accentuated by use of unsuitable solvents. Vehicle compatibility and rate of evaporation must be controlled through the use of proper thinners. The use of at least a portion of slow-evaporating thinner, such as kerosene or heavy mineral spirits, is desirable from the standpoint of avoiding too short lap time.



Paint consistency also has a direct influence on ease of brushing. Unless the system is highly flocculated, a heavy-bodied paint is likely to be hard to brush. Flocculated systems offer decidedly less resistance to spreading than systems in which this structure does not exist. Ease of brushing may therefore be greatly enhanced by the addition of small quantities of water. An efficient way of introduction is in the form of mild soap solutions. The tendency to flocculate is far greater in poor wetting systems than in good wetting systems. The introduction of stearates also contributes to good brushing.

**Leveling.** Improved leveling may be accomplished by (a) use of bodied oils, (b) control of acidity, and (c) proper selection of extenders.

Bodied oils yield better flowing tendencies than the raw or refined (unbodied) oils. The latter show a decided lack of flow. Of the commonly used bodied oils, fish oil shows significantly inferior properties in this respect. Oxidized (blown) oils invariably possess better leveling properties than polymerized (kettle-bodied) oils. Varnishes also vary in this property, depending upon the constituents and method of processing.

Highly acidic vehicles are conducive to poor leveling which may be remedied by partial neutralization of the acids present. The reaction products formed may serve as a further stimulant to leveling.

The magnesium silicate type of extenders also curtails leveling, which is not characteristic of the calcium carbonates. The general tendency of the stearates is also toward reduced leveling, especially if an excessively gelled structure is produced in the paint system.

**Enamel Holdout.** The ability of flat paints to hold out subsequent coats of enamel is a function of pigment concentration and the oil requirements of the pigment content involved. In order to construct a paint system that will yield an impervious film, sufficient binder must be used to satisfy the oil demands of the pigments present. Figure 8 depicts graphically the relationship of enamel holdout of the same three paint systems referred to in Figs. 4 and 5. The systems which yielded highest dry film hiding power at low binder contents show the greatest deficiency in enamel holdout properties. Furthermore the holdout properties of all three systems improve in direct proportion to the amount of binder present per unit volume of pigment, up to a point where maximum holdout properties are attained. Based on all available evidence, enamel holdout properties are directly related to dry film hiding power.

Figure 9 demonstrates the enamel holdout properties of these same three systems containing 1 per cent water based on total paint volume. Generally the systems were affected adversely and in a manner directly proportional to the degree of water sensitivity. Paint *A*, for example, showed the highest dry film hiding power and, owing to the

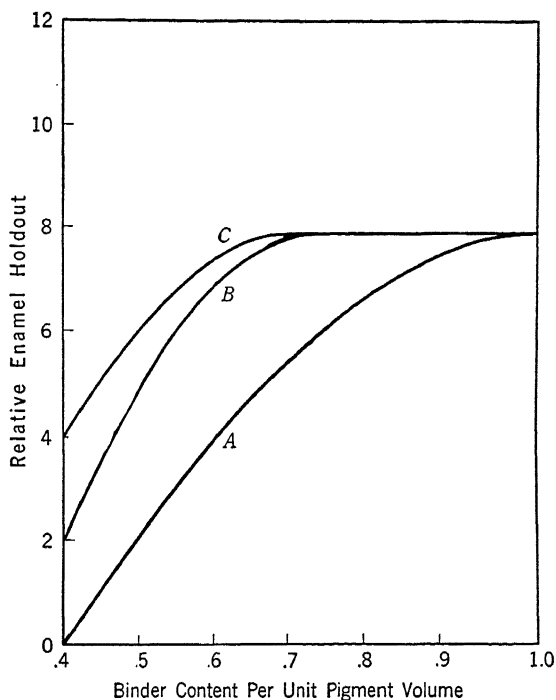


FIG. 8. Enamel Holdout (without Water).

hydrophilic nature of the pigments present, showed the greatest amount of consistency increase due to flocculation when water was added. This paint also showed poor enamel holdout.

**Washability.** Degree of stain removal and the ability of the film to withstand the necessary abrasive action during scrubbing constitute a measure of the washability characteristics of a paint film. Type of vehicle used and film hardness influence this property which is closely related to enamel holdout. At the same time there are other factors which have a direct bearing on the washability characteristics of a film for a given vehicle system, which may be summarized as follows:

High consistency (high dry hiding) pigments yield films possessing significantly poorer washability than the low and medium oil absorption pigments.

Within certain limits, washability is directly proportional to the amount of binder present per unit volume of pigment.

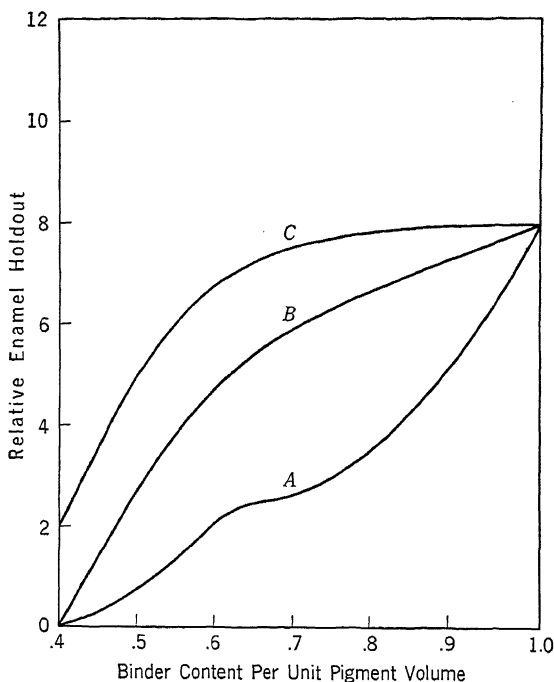


FIG. 9. Enamel Holdout (with Water).

Low binder content produces a tendency toward poor washability regardless of the pigments used. Sufficient binder is required to satisfy the oil demands of the pigments before good washing characteristics are obtained.

The addition of water to a paint results in inferior washability depending upon the degree of flocculation obtained.

### Semi-Gloss, Gloss Paints, and Enamels

Semi-gloss, gloss paint, and enamel systems are so closely related to one another that for the purpose of this discussion they may be considered as one group. They may be very similar in composition as well as in paint and film properties. The essential difference, as indi-

cated by their designation, lies in their ability to produce varying degrees of luster in the dried film.

Film surface effects, such as gloss, may be governed by the amount of binder present per unit volume of pigment.

According to results of the Golden Gate Paint and Varnish Production Club (6) there is no definite point where all gloss paints reach maximum desirability. In general it was found that beyond 40 per cent pigment concentration by volume the gloss diminished rapidly.

Pickett (18) has also found that, regardless of the pigment, the gloss of an enamel is closely related to the binder-to-pigment ratio by volume. It was also found that the ratio will vary somewhat, depending upon the nature of the binder. In the varnishes, little difference was observed with varying oil lengths. In the alkyds some variations were observed. Other types of vehicles or binders behave in a regular manner but may be slightly different from the varnishes. It was found that the volume ratio could be lower with a bodied linseed oil than with either varnish or alkyd and yet yield a high-gloss enamel.

At the same time, the opaque pigments and other formula constituents are not without influence. As indicated earlier in the chapter, the semi-gloss paints fall between the flat and gloss paint systems in pigment concentration, and the enamels are usually characterized by higher binder content.

The limits for either group are not sharply defined and are subject to variation, depending upon major formula components and specific film properties desired.

Another distinction that usually exists between gloss paints and enamels is a matter of consistency and leveling properties. Enamels are characterized by less body and better leveling tendencies by virtue of the lower pigment volume concentrations which are required to produce them. Pigment concentrations are restricted and extenders are normally precluded by the high gloss requirements of enamels. Titanium dioxide can be used to great advantage in conforming to these requirements.

The choice of vehicles for this group of paints is very large and is usually governed by cost limitations coupled with performance requirements. The different types of vehicles show wide diversity in inherent properties, which are discussed in Chapter 8.

Some of the influential factors governing the physical properties of gloss paints and enamels are closely related to those for flat paints and will not be given further consideration here. They will be dis-

cussed only in so far as specific application to these products is concerned.

**Consistency.** The factors which govern this property are very similar to those for flat paints. Until recently, high consistency pigments suitable for gloss paints were rather limited on account of their gloss deficiency. Fine-textured pigments are now available, however, which can be used for increased consistency without detracting from the gloss.

Typical gloss paints usually run higher in consistency than the enamel products, which is accounted for by the fact that the gloss requirements are not so high and the nature of the vehicles used permits higher pigmentation.

Bodying agents most frequently resorted to in connection with gloss paints consist of overbodied wood oil varnishes or extremely heavy-bodied poor wetting oils. There are also some proprietary commodities commercially available which behave in a similar manner. Their action is based on flocculation of the system, and the quantities that can be used are limited because of the fact that when used in excessive amounts they may have a deleterious effect on gloss.

Their effectiveness depends upon the wetting efficiency of the vehicle system involved. In extremely well-wetted systems the effect may be negligible, whereas in systems of moderate wetting efficiency significant increases in consistency occur.

The use of water is not recommended as a bodying agent for gloss paints because of its adverse effect on gloss in most systems.

The use of stearates is also prohibited in most cases by virtue of their tendency to reduce gloss. Some of the palmitates may be used in limited quantity with less dulling effect.

**Suspension.** Vehicles play a very prominent part in the suspension of gloss paints and enamels largely by virtue of their different wetting characteristics. No attempt will be made to classify them because of the many variable factors involved. It may be generally assumed, however, that vehicles with extremely good wetting characteristics usually show poor suspending properties because of the lack of structure in the system.

The use of bodying liquids frequently improves suspension, usually in proportion to the increase in consistency obtained.

**Opacity.** Again a definite relationship exists between hiding power and ratio of binder to pigment by volume. The effect is not so pronounced as for flat paints, and the results indicate that there may be a critical point at which maximum hiding power efficiency is obtained for a given system. The relationship is similar to that of flat paints

in that it is subject to variation, depending upon the type pigment used, the pigment concentration by volume, and the vehicle involved.

In the gloss paint range, pigment hiding power efficiency varies inversely with pigment concentration. Increasing the concentration of the pigment decreases pigment efficiency and may cause less increase in paint hiding power than might be anticipated. Obviously this relationship is subject to variation based upon the composition of the system involved. Furthermore the increase or decrease in hiding power is not a straight line function. Maximum efficiency is obtained at the lower pigment concentrations.

**Color.** By virtue of the higher ratios of binder-to-pigment volume used in gloss paints, the color of the vehicle used has a very pronounced influence on film color. For good color, pale vehicles must be used. Also, pigments offering maximum color and brightness, such as titanium dioxide, are preferable where film color is a factor.

Where color retention is a factor, titanium pigments are again preferred as offering maximum resistance to color change. Zinc oxide is also noted for its color retention value and has been found effective in improving color retention of paint systems when used in conjunction with other pigments.

**Gloss.** Not all opaque pigments behave similarly in their gloss producing and gloss retention properties. Conversely, vehicles also differ in their ability to produce glossy films. Despite this fact, however, the most prominent factors which influence the amount of gloss (image reflectivity) exhibited by a paint film are the ratio of binder per unit volume of pigment and the state of pigment dispersion attained in the system. With ample binder to satisfy the pigments and a well-dispersed system, good gloss will result.

The control of gloss in the semi-gloss products requires more exact manipulation of the formula. Excessive binder content must be avoided to keep the inherent gloss within range. Flatting extenders are frequently employed in whatever amounts necessary to produce satisfactory gloss requirements. Other flatting agents, such as stearates, may be used for the same purpose.

Zinc oxide is used in some products to enhance gloss as well as improve hardness. When used in conjunction with titanium dioxide or with a combination of titanium dioxide and antimony oxide, hazing may result in the film. This may be partly remedied by using a colloidally fine zinc oxide, elimination of lead drier, and by the incorporation of a small percentage of a high-solvency thinner, such as pine oil.

The use of water should generally be avoided in gloss paint systems because of the deleterious effect it may have on gloss. Some of the

poorer wetting systems may show flocculating tendencies when water is added, accompanied by a considerable drop in gloss. The effects of adding various amounts of water to several paint systems are depicted in Fig. 10. These paints differ only in the type of prime pigments used. The loss of gloss is rather pronounced as increasing

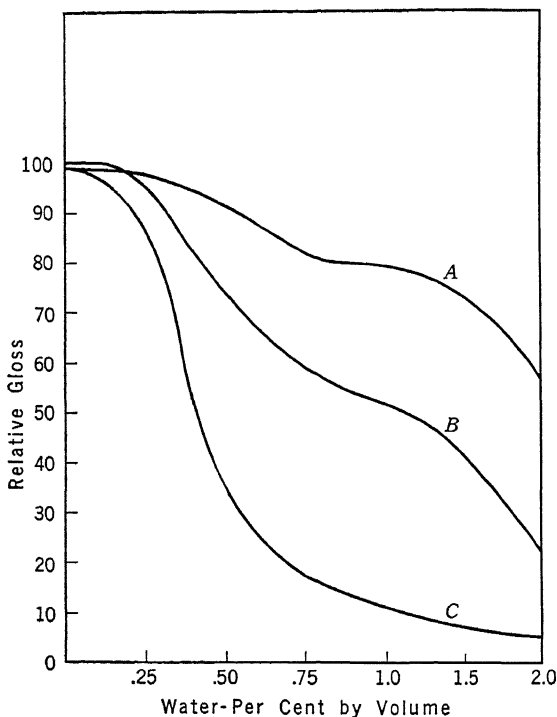


FIG. 10. Effect of Water on Gloss.

amounts of water are added and varies for the different systems as indicated.

**Leveling.** In gloss paint and enamel systems, leveling and sagging are closely related. Quite frequently, too, much flow is encountered, which results in sagging when the paint is applied to a vertical surface. In this type of product, therefore, the usual problem is to prevent excessive flow rather than promote it. This may be accomplished by building up a certain amount of gel structure in the system. Too much structure will reduce leveling. Inasmuch as leveling and sagging are so closely related it is often necessary to compromise on these properties.

The bodying agents described for consistency control are usually quite effective in preventing sagging without retarding the leveling to an objectionable degree.

Leveling may also be influenced by the prime pigments involved. The surface-treated pigments may have a pronounced effect on flow, usually in the way of retardation.

Vehicles with good wetting characteristics produce deflocculated systems which have free flowing tendencies frequently resulting in sagging. The replacement of tung oil in varnishes with some of the more limpid and softer drying oils yields vehicles of superior wetting power. These products often promote excessive flow resulting in sagging tendencies.

### FORMULA COMPUTATION

#### Nomogram

The computation of pigment-to-binder relationships can be facilitated by using a suitable nomogram.

The following example, which comprises a combination of three or four common calculations met in paint formulation, will serve to explain the normal use of the attached nomogram.

*Data:* A paint of 15 pounds gallon weight, with a pigment-vehicle ratio of 65/35 by weight. The vehicle has a gallon weight of 8 pounds and contains 60 per cent non-volatile by weight. Volatile component consists of mineral spirits of 6.5 pounds gallon weight. To find:

1. Per cent non-volatile by volume in vehicle (% NV).
2. Pigment-binder ratio (P/B).
3. Pigment volume (PV).
4. Pigment content (pounds pigment per gallon of paint).

*Operations and calculations* (Roman numerals refer to alignments indicated on small explanation nomogram):

1. Vehicle computation: (I) Align  $P = 6.5$  lb. with  $T = 8$  lb.; read 5.21 on  $A$ . (II) Align  $W = 60\%$  with  $A = 5.21$ ; read 50.7% on  $V$ . This is the % NV by volume in the vehicle.

Paint computation: (III) Align  $P = 8$  lb. with  $T = 15$  lb.; read 3.81 on  $A$ . (IV) Align 65% on  $W$  with 3.81 on  $A$ ; read 34.4% on  $V$ . This is the % pigment by volume in the paint.

2.  $100 - 34.4 = 65.6\% = \%$  vehicle by volume in paint.  $65.6 \times 50.7 = 33.3\% = \%$  binder by volume in paint.  $P/B = 1/\frac{33.3}{34.4} = 1/.969$ .



$$3. \text{ PV } \frac{34.4}{34.4} + 33.3 = 50.8\%.$$

4. Pigment content =  $W \times T = 0.65 \times 15 = 9.75$  lb. pigment per gallon of paint.

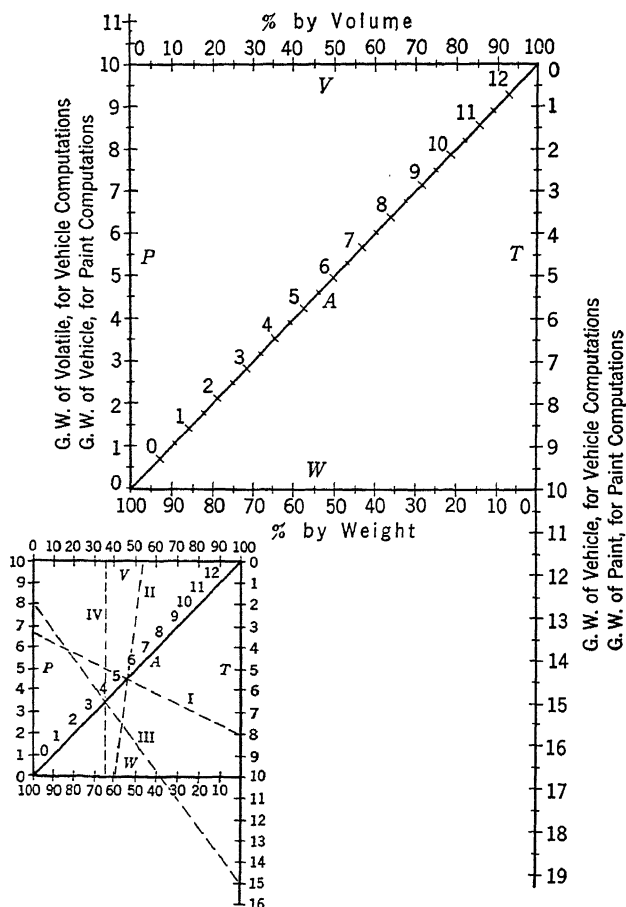


FIG. 11. For explanation see instructions, page 383.

The *A* scale is merely a “carry-over” scale between *P* and *T* to *W* and *V*, and is marked off in arbitrary divisions.

The change in the definition of the scale values of *P* and *T* for the two computations is unavoidable. It will be found, however, that no confusion will result if the following rule is adhered to:

Of the two gallon weights used in any computation, the gallon weight of the lowest magnitude will always be placed on the *P* scale.

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## ACKNOWLEDGEMENT

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## CHAPTER 12A

### MARINE PAINTS

NEIL T. PHELPS and LAWRENCE F. DORATO

"Make thee an ark of gopher wood; rooms shalt thou make in the ark, and shalt pitch it within and without with pitch."

*Genesis, 6: 14.*

### INTRODUCTION

#### History

In the early days, the Greeks and Romans used metal sheeting to protect the wooden hulls of their boats from the boring worms (1). In the eighteenth century, copper sheeting was used extensively for the protection of wooden hulls against both boring worms and marine fouling. When iron hulls were first used, considerable difficulty was encountered because of the galvanic action between the copper sheeting and the iron hulls. An attempt was made to insulate the copper sheeting from the iron hulls by the use of an anti-corrosive paint, which was applied directly to the hull. This treatment was effective in reducing the galvanic action. The iron used in ships' hulls in the latter part of the nineteenth century was of a different type from that commonly used today, and there is considerable evidence that the older type of iron had greater resistance to corrosion, which resulted in less exacting requirements for an anti-corrosive paint than the requirements of the present day. Furthermore, the chemical effect was much less at that time than it is today, with the chemical wastes of large industries finding their way into the harbors. A further difference in the requirements for bottom paints results from the greater speeds of today which require a paint having higher resistance to the strong erosive action.

A patent showing the general composition of bottom paints for early ships was granted to William John Hay of Lymington Lodge, Southsea, England (6). This patent covers a process for treating oxides of copper and other metals for keeping ships' bottoms or other structures free from animalculae and other animal and vegetable matter. Ac-

cording to the patent, Hay ground the black or protoxide of copper (cupric oxide) in linseed oil, then boiled the mixture, and thinned it with turpentine. It is stated that, when using this type of coating on iron, "one or two protective or non-conducting coats should be first applied. This may be red or white lead paint or asphalt varnish, etc." A paint called McIness's was introduced about 1860. It was composed of a rosin varnish, iron oxide pigment, and an anti-fouling metallic copper soap. This paint was of a heavy consistency and required heating for its application. In 1871, John Rahtjen patented an anti-corrosive primer which consisted of a mixture of shellac, Stockholm tar, linseed oil, and iron oxide; also, an anti-fouling paint similar to the anti-corrosive primer, with the addition of mercuric oxide and arsenic. This material is basically similar to materials being used at the present time. With the increased use of steel replacing wrought iron for ships' hulls (by 1912 wrought iron for hulls had practically disappeared), the corrosion problem became much more serious, requiring anti-corrosive bottom paints which would provide better protection. The bottom paints formulated at this time were the forerunners of the modern anti-corrosive and anti-fouling paints.

### Economical Aspects

It has been estimated that fouling on a ship's bottom may reduce the maximum speed as much as 25 per cent, which will result in a 30 per cent increase in fuel consumption to maintain normal cruising speed (1). Freighters which are required to remain for some length of time in brackish harbors are subject to ideal fouling conditions. As much as 100 tons of fouling have been removed from the bottoms of such boats. The use of poor quality paint, where fouling conditions are bad, will result in heavy fouling within a short period of time, whereas good ship bottom paint will prevent bad fouling for four to five times as long a period.

The results of a test made on a navy vessel are reported by Adamson (1): "A vessel of a type of major importance had reported vibrations which at high speed caused fire control instruments to be useless, dishes would not remain on tables in certain parts of the vessel, at other parts of the vessel, conditions were 'uncomfortable.'" The investigation required placing the vessel in drydock, and a run of approximately 300 miles to the drydock was made. During the run, engineering data were taken. In drydock, approximately 200 tons of fouling (barnacles and hydroids) were removed. Nothing of consequence was found wrong with underwater parts. The bottom was

cleaned and painted and the vessel again run over the same course. The vibrations were practically eliminated by removal of the fouling. The data showed the following effects of the fouling on the bottom:

1. Displacement increased 194 tons.
2. Fuel consumption—gallons per mile—increased 44 per cent.
3. Decrease in speed at 136 r.p.m. (propeller speed) 1.45 knots.
4. Increase in horsepower at 136 r.p.m. (propeller speed) 26 per cent.
5. Decrease in speed at 298 r.p.m. (propeller speed) 5.63 knots.
6. Increase in horsepower at 298 r.p.m. (propeller speed) 18.2 per cent.

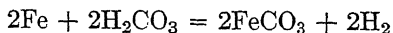
In addition to the increased fuel consumption and possible loss of time resulting from heavy fouling growths, the loss resulting from corrosion is a highly important factor. It has been estimated that up to 2 per cent of the world's tonnage of iron may be replaced yearly, owing to the results of corrosion and, when it is considered that the world's production of iron and steel was approximately 1,200,000,000 tons for 1931, the losses resulting from corrosion run into millions of dollars per year.

#### DESTRUCTIVE AGENCIES

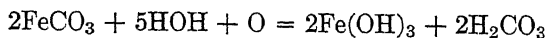
##### Corrosion

Several theories have been advanced to explain the process of corrosion. Probably the earliest was the carbonic acid theory. The essential hypothesis of this theory held that the interaction of oxygen with iron to give iron oxide (rust) was not possible without the presence of carbonic acid.

Treadwell and Hall (11) state that the process of rusting is a cyclical one, and three factors play an important part—first, an acid; second, water; and third, oxygen. The process of rusting is always started by an acid (even the weak carbonic acid suffices), and the acid changes the metal to a ferrous salt with the evolution of hydrogen as expressed by the following equation:



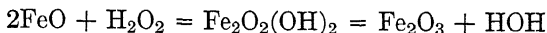
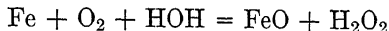
Water and oxygen now act upon the ferrous salt, causing the iron in this salt to separate out as ferric hydroxide, setting free the same amount of acid which was used in forming the ferrous salt:



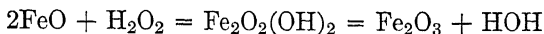
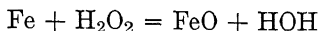
The acid which is set free again acts upon the metal, forming more ferrous salt, which is again decomposed, forming more rust. A very

small amount of acid, therefore, suffices to rust a large amount of iron. If the acid is lacking, the iron will not rust. If we desire to prevent this rusting, we neutralize the acid, e.g., add milk of lime. Iron remains bright and clear under an alkali.

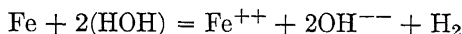
Later, the peroxide theory was advanced by Traube (10). According to this theory, oxidation proceeds along the scheme as indicated by the reactions:



The excess of hydrogen peroxide reacts with an additional amount of iron to form more iron oxide, as shown by the following equations:



The modern theory is the *electrochemical theory*, which was evolved from the electrolytic theory (5). This is the most satisfactory of the theories advanced and the most generally accepted. According to this theory, the primary reaction in the rusting of iron is between iron and water, expressed in the following equation:



The ions Fe and 2OH then combine to form ferrous hydroxide  $[\text{Fe}(\text{OH})_2]$ . This is further acted upon by oxygen and moisture and forms the complex substance known as iron rust. It is evident that the composition of rust will vary according to the conditions of its formation.

This theory, of course, is based on the fact that iron has a definite tendency to pass into solution as iron ions, electrically charged, and then can be oxidized from the ferrous to the ferric state. Once started, it is obvious that the extent to which this reaction will proceed and the rapidity with which it will reach its end point depend on several factors, important among which is the time element. Time is mentioned in particular because it is a rate factor which is often minimized or omitted in considerations; but when one calls to mind that in the field of protective coatings we are dealing with breakdowns which occur anywhere from six months to six years, it readily becomes obvious that the small, almost negligible effect over a period of a few days is more than compensated for when spread over the life of a paint film. In other words, we have a minute force, unimportant as

it may seem, incessantly at work over a long period of time until the failure occurs which cannot be ignored.

That iron dissolves in water is a known fact and has been demonstrated experimentally. When iron dissolves, hydrogen is liberated. Hydrogen is liberated as a gas and, in this state, is found dissolved in water until it has had a chance to react with some dissolved oxygen or may have reacted with some other substance in the water. If the water has an abundance of hydrogen ions, we may then see the actual liberation of hydrogen as a gas and, in this category, we can cite the reaction that visually takes place when a piece of iron is suspended in some water to which has been added a few drops of an acid (concentration of hydrogen ions) such as hydrochloric or sulfuric acids.

In the ordinary cases, in the absence of high acidity or concentration of hydrogen ions, some polarizing action of the hydrogen is experienced and, for a time, the reaction is slowed down considerably. Eventually, however, the iron compounds, being but only very slightly soluble, are removed from the sphere of action, thus upsetting the equilibrium and allowing the procedure of the reaction.

Iron, then, goes into solution, is oxidized to ferrous or ferric hydroxide, and is precipitated in the form of greenish or brownish "rust." Removal of this reaction product from the sphere of activity allows the reaction to proceed and so removal has a definite effect on the rate of corrosion.

Where the hydrogen acts as a polarizer, the iron having passed into solution, we notice a speeding up of the reaction if hydrogen is removed through interaction with dissolved oxygen. It has been found that corrosion is accelerated when any substance that reacts with hydrogen is present. We begin to notice rusting due to the formation of complex hydroxides of iron which come out of solution, and the reaction is apparent as corrosion proceeds.

As is well known, corrosion is rarely seen as an evenly distributed reaction product. On the contrary, it is most evident as certain irregular areas and patches over various sections of the affected surfaces. One of the most common manifestations of corrosion is a segregated or localized form commonly described as pitting. It is easily recognized by its speckled appearance and, also, by the fact that the affected areas are small compared to the whole surface. Corrosion products are in evidence at the pits. Pitting is due to many factors, chief among which are the difference of potential of the surface of the metal, which may be due to inhomogeneity of the metal, inclusion of different metals giving rise to galvanic action, and differences in poten-

tial of the metal arising from the strains of varying natures and magnitudes. This latter cause is often noticed in failures at rivets or welded joints.

Pits are often formed by the incomplete covering of a protective film such as mill scale ( $\text{Fe}_3\text{O}_4$ ) which is cathodic to iron. In this case, the areas not covered by scale are subjected to the corroding influence until pits are developed. In the vicinity of riveted or welded areas, there is often present a strain in the metal and although, by itself, strained metal may not be more subject to corrosion than unstrained metal, nevertheless when it is in contact with metal not under strain, difference of potential is set up and the strained metal is anodic to the unstrained metal and pitting or segregated corrosion develops.

Pitting also results from the contact of copper and brass fittings with the underwater portion of the hull. This type of corrosion is most generally found in the vicinity of the hull adjacent to the propellers. It is possible to minimize this type of corrosion by the installation of zinc plates on the hull. The zinc being higher in the electromotive series than iron, it goes into solution instead of the iron. The zinc plates gradually waste away and require renewal from time to time. A test was made substituting a mild steel for the zinc and, although the mild steel had a longer life than the zinc, the difference in potential between the hull plates and the steel plates was not sufficiently great to prevent the pitting of the hull plates.

### Fouling

Fouling is the attachment of minute animal and vegetable organisms to the bottom of both steel and wooden vessels. On wooden hulls, destructive marine boring animals are encountered. These animals belong to groups according to their varying and characteristic methods of attack. The molluscan borers enter the timber as minute larvae and burrow and grow at the same time, but do not enlarge the hole of entrance. The result is that the interior of timber infested by them may be thoroughly honeycombed without exhibiting any evidence from the outside except for the minute holes which are seen with difficulty by the naked eye. The size, shape, and character of the borers vary widely within the different genera.

The wood-boring Crustacea run shallow galleries just beneath the wood structure but, since these animals are found in great numbers, their work destroys the outer layers of the wood, which is washed away and a new surface exposed and subjected to attack. This damage can readily be seen on inspection; damage resulting from the



activities of the Mollusca easily escapes notice and is, therefore, more dangerous.

It has been found that, although the parasites collecting on a ship's bottom belong to several thousands of species, they can be divided into two general classes: barnacles and hydroids (1). The barnacles are the animals which form the hard shell-like structures on the ship's bottom. Some species of barnacles are found over wide areas; other species are found only in restricted areas. The animal inside the shell is fed by putting out feelers and, by this means, grasps the microscopic organisms which it feeds upon. The shell increases in size and is firmly cemented to the ship's bottom. When the barnacle has reached this stage, it is too late for it to be affected by a toxic anti-fouling paint. Although the barnacle may be killed by remaining in fresh water for 48 hours, the shell structure will still remain on the bottom of the vessel and will afford a better surface for the attachment of new organisms. The only way to remove the shell is by mechanical scraping.

The hydroids, which appear as grasslike fibers, are often called grass but are actually animal. Like the barnacles, there are numerous types varying in size and character. The fouling organisms become attached while the vessel is not in motion. Therefore, a boat which is not required to remain in fouling waters for longer than 24-hour periods will be practically free from fouling. Once the organism has attached itself to the bottom, its growth is not materially affected by the movement of the vessel.

### **Erosion**

Erosion is caused by the motion of the vessel through the water and, in the case of coating materials used on superstructures, results from the effect of sun, rain, and splashing sea water. Artificial erosion results from frequent scrubbing and washing with strong soaps and abrasives.

### **Chemicals**

The chemical action of polluted waters in certain harbors is very pronounced and has a decidedly detrimental effect on certain types of paints which are not formulated so as to be chemically resistant. Certain types of cargoes often require interior paints having a high degree of chemical resistance. For certain uses, such as the coating of the interior of cargo tank ships, coatings are required to withstand

the most severe conditions of corrosion and immersion in liquids such as gasoline, sour crude oils, salt water ballast, and crude vegetable oil.

### **Natural Weathering**

The effect of natural weathering is more severe on marine paints because of the extreme temperature changes and exposure to salt-laden atmosphere, sun, wind, and rain. Consider, for example, the weather conditions encountered by a tanker plying between Houston, Texas, and Boston, Mass., in midwinter. The vessel leaves Houston in humid, mild weather, temperature 75°. These conditions maintain until the tanker leaves the Gulf Stream. It runs into heavy seas off Cape Hatteras, with cooler weather. As it moves northward, it encounters freezing temperatures and, by the time it reaches Boston, it is coated with several inches of ice. What accelerated test cycle is more severe than this?

## **FORMULATION**

### **Bottom Paints**

Under this heading are included three separate and distinct types of coating materials for use on steel hulls and two types of coatings for use on wooden hulls. The paint which is first applied to the steel bottom of a vessel is called an anti-corrosive paint or Ships' Bottom No. 1 Coat. There is considerable variance of thought and opinion as to the proper formulation of an anti-corrosive bottom paint. This subject is considered here from the standpoint of the requirements of anti-corrosive paint and what pigments and vehicles can be combined to produce a paint meeting those requirements.

First and most important, an anti-corrosive paint must reduce corrosion to a minimum; second, it must dry rapidly; third, it must provide a suitable surface for succeeding coats; and, fourth, it must have good resistance to erosion. It might be mentioned here that some technologists have believed it necessary to use an anti-corrosive paint of such a nature that it will gradually wear off or "exfoliate." This opinion, however, does not hold to any great extent at the present time. On the contrary, it is felt that a hard, tough, water-resistant, anti-corrosive paint is to be desired.

Protection is afforded to a ship's bottom either by mechanically excluding the corrosive agencies, by chemically inhibiting the corrosion action, or by a combination of both. Generally speaking, mechanical

protection is secured through the proper formulation of the vehicle and chemical inhibition of the corrosion action is the result of the proper selection of pigments.

The fact that no known paint film is entirely impervious requires the maximum efficiency in corrosion-inhibiting properties of the coating material.

Numerous pigments have been tested and recommended for use in anti-corrosive primers. These pigments include chrome yellow, zinc yellow, zinc oxide, zinc powder, basic lead chromate, red lead, iron oxide, and blue lead (8, 9). Various investigators have tested the efficiency of these pigments for use in anti-corrosive paints and varying results have been reported. It is stated that chrome yellow, basic lead chromate, red lead, blue lead, and iron oxide have no chemical inhibiting effect on the corrosion reaction. Zinc yellow and zinc dust are claimed to have a positive inhibiting action. Zinc yellow in the presence of moisture forms the chromate ion which acts as the inhibitor. In the case of the zinc dust, the zinc being higher in the electromotive series has a tendency to go into solution in preference to the steel of the ship's bottom. Zinc yellow is not generally recommended for use in anti-corrosive paints for ships' bottoms, owing to the fact that, because of its solubility, it is likely to cause blistering. The proper choice of vehicle to use with the zinc yellow pigment is, however, an important angle to be considered.

All the other pigments have been tried in anti-corrosive paint formulations with varying degrees of success. Although the chrome yellows (lead chromate) contain the chromate radical, they are not sufficiently soluble in water to form the necessary corrosion-inhibiting chromate ion. Red iron oxide has been used in considerable quantity because of its cheapness, its color, and its toughening effect on the vehicle. Several investigators have reported unfavorable results with red lead.

Zinc powder is usually used in combination with zinc oxide, and favorable results have been secured with this pigment combination; although it is claimed that the zinc dust is too rapidly dissolved, resulting in short effective life. However, it is quite possible that the use of a vehicle of improved water resistance might prolong the effective life of a zinc dust-zinc oxide paint.

Vehicles commonly used in this type of paint have been very poor in water resistance, and, in fact, it was believed that to be satisfactory a vehicle of this type was required. More recent results of tests on

anti-corrosive primers for use under water indicate that a very satisfactory anti-corrosive paint can be prepared with zinc yellow in combination with other pigments, using a vehicle of the medium oil length spar varnish type (8).

A commonly used vehicle of the present-day anti-corrosive paints is a combination of rosin, coal tar, manganese linoleate, and thinners. Formulations used by the navy some years ago contained vehicles composed of shellac and pine oil thinned with alcohol (1). The shellac vehicle was replaced by the rosin vehicle because shellac was imported and was also considerably higher in price than rosin. Reports have also been made of the use of chlorinated rubber vehicles which indicate interesting possibilities for future formulations (3). The chlorinated rubber vehicle has exceptional chemical resistance and forms a tough, water-resistant film.

### Anti-Fouling Paints

The anti-fouling paint, sometimes called Ships' Bottom No. 2 Coat, is used on both steel and wooden hulls. There is some slight difference in the formulation for the different types of hull construction, but the basic principles followed are the same. The anti-fouling paint is applied to the bottom of the vessel below the water line. Usually two coats are used. The essential requirement of an anti-fouling paint is that it prevent the growth and collection of marine fouling organisms. The use of a toxic ingredient in the anti-fouling paint is the most effective means of preventing the growth of these fouling organisms. Numerous materials have been tested as the toxic ingredient for anti-fouling paints. This list includes cuprous oxide, mercuric oxide, naphthalene, sodium hydroxide, thymol, hydroxylaminosulfate, strychnine sulfate, chinium sulfate, uranium nitrate, hexamethylene-tetramine, tobacco powder, pyrethrum powder, sodium silico fluoride, nicotine sulfate, chromium oxide, brucine, saponine, pikrotoxines, acetic acid, tungstic acid, fluorides, and nitro and chlorine compounds of phenol, arsenic, Paris green, etc. (2, 7). Out of this entire list, there are only two or three materials which are appreciably toxic to marine growths and useful in anti-fouling paints. The most effective material is mercury oxide, with cuprous oxide second best. Practically all the most efficient anti-fouling paints used today contain a combination of mercuric oxide and cuprous oxide. Sometimes a small percentage of arsenic and/or Paris green is also used. It has been reported that the following ratios of copper to mercury are effective (2):

25 ounces of copper to  $1\frac{1}{2}$  ounces of mercury in northern oceans.

20 ounces of copper to 5 ounces of mercury in southern oceans.

14 ounces of copper to 14 ounces of mercury in tropical waters.

The anti-fouling mixture generally used is 14 ounces of copper to 7 ounces of mercury.

In addition to the toxic materials, other pigments, such as iron oxide, zinc oxide, and various extenders, are employed to secure proper body and other physical characteristics of the paint. For a number of years, the vehicle used in anti-fouling paints was composed of shellac, pine tar, and alcohol. More recently, a vehicle composed of rosin, coal tar, manganese linoleate, and coal tar naphtha has been used. Some mention has also been made of the use of chlorinated rubber as the vehicle. However, there is no definite information available as to the results secured with this type of vehicle. There have been numerous attempts to compound materials which are quite different in their makeup from the normal run of anti-fouling paints. An example of this is a ship's bottom paint patent by Giuseppe Capurro (4). The paint made according to this formulation has the following composition:

Refined coal tar.

Sulfur.

Resin (probably rosin).

Paris green.

Benzol.

This paint is claimed to have both anti-corrosive and anti-fouling properties. Tests made, however, do not indicate that this composition is especially efficient.

It is only natural that technicians have made numerous attempts to combine the anti-corrosive and anti-fouling paints in one formulation. Attempts to do this have not been particularly successful. A combination paint, which is reported to give fairly satisfactory results, is composed of yacca resin, pine oil, alcohol, petroleum ether, zinc oxide, silica, blanc fixe, zinc dust, Paris green, and mercuric oxide (1). Some authorities believe that a good anti-fouling paint should be of such a nature that, in addition to containing toxic pigments, it will gradually be worn away by the action of the sea water. It is questionable whether or not a definite attempt has been made to formulate a vehicle which will do this. It is necessary, of course, that the vehicle for anti-fouling paint be, to some extent, water-permeable

because the toxic effect of the paint depends on the slow dissolving of the copper and mercury oxides. Experimental formulations have been tested, using a short oil phenolic vehicle, and it has been found ineffective because the vehicle was too waterproof to allow the necessary dissolution of the toxic ingredients.

An anti-fouling paint in which pure electrolytic flake copper is dispersed in a six-gallon tung oil coumarone indene *p*-phenylphenolformaldehyde vehicle is reported as having satisfactory anti-fouling properties (12). However, there is considerable work yet to be done on the use of such a formulation as an anti-fouling paint. It should be a satisfactory material for wooden bottoms, and, in fact, copper paints have for some time been widely used for this purpose.

The subject of anti-fouling paints offers great possibilities for future research, and it is more than likely that important progress will be made along these lines in the near future.

### **Boot-Topping and Topside Paints**

The boot-topping paint is applied to the hull of the vessel between the light load and the deep load line. The conditions of exposure are particularly severe and are similar in nature to tide-level exposure, with erosion and abrasion added for good measure. The topside paint is applied to the hull above the deep load line. Both boot-topping and topside paints are subjected to wind, water, sun, erosion, and other destructive agencies in alternating cycles, and it can readily be appreciated that these coatings must be carefully formulated to give the desired service. Although called paints these materials are actually enamels, since the type of vehicle commonly used is a medium to long oil spar varnish. Phenolic resins with tung oil in 35- to 50-gallon oil lengths make very excellent vehicles for boot-topping and topside paints. With the shortage of tung oil, the soft drying oils have been used in shorter oil lengths with phenolic resins to produce satisfactory vehicles for these paints. A considerable quantity of natural resins, such as congo, batu and east india, have been used in these spar-type boot-topping and topside vehicles. Within the last few years, considerable attention has been given to the use of waterproof alkyd resins as boot-topping and topside vehicles, and results indicate that the alkyd resin vehicles, when properly handled, give outstanding service. The pigments used in these paints are almost unlimited, selection being determined by the color desired and the exterior durability characteristics such as light fastness, chemical inertness, and chalking resistance. Pigments used include carbon black, lampblack, iron oxides, chrome

greens, chrome yellows and oranges, chromium oxide, and various types of chalk-resistant titanium dioxides.

### **Deck and Superstructure Paints**

The paints included under this heading are formulated along the lines of standard industrial protective paints, with attention being paid to the type of exposure involved. The primers usually contain a fairly high percentage of zinc yellow pigment in conjunction with other colors, such as red oxide and inert extenders. Red lead is also quite commonly used in primers for this purpose. The primer vehicle is a medium oil length spar varnish or alkyd resin. The finish coats belong to the class generally referred to as deck paints. In this type of material, vehicles are similar to those used in the primer, and the pigments depend on the color desired and, in general, belong to the same class of pigments as those for boot-topping paints.

### **Interior Paints**

Paints used aboard ship for interior work are essentially the same as those found on the market for general interior work. There is, however, one important factor to be borne in mind, and that concerns the exposure to which marine finishes are subjected. It is found that these finishes are subjected to more severe treatment than ordinary household paints because of frequent scrubbing with strongly alkaline soap with little regard to the effects of these cleansing agents on the finish. This type of treatment, of course, necessitates finishes formulated to resist the physical and chemical action to which they are submitted. The type of vehicle used in these paints may be a medium oil length spar or alkyd resin.

Chlorinated rubber has also found use in interior marine paints because of its fire-retarding property and its chemical resistance. In this connection, fire retardants may be added to the usual interior marine paints.

### **Finishes for Special Uses**

Included in this class are spar varnishes, stack paints, special heat-resisting paints for use in engine rooms and boiler rooms, and special coatings used in various types of cargo tanks. The use of spar varnish is confined mostly to pleasure craft and small racing boats. The varnish used for this purpose should be of the best quality obtainable. Medium to long oil varnishes using the 100 per cent phenolic resins probably represent the highest type of quality obtainable. Smoke

stack and heat-resisting paints are formulated with pigments and vehicles which are the least affected by elevated temperatures.

Particularly in engine and boiler rooms, where the temperature is rather high and where practically all illumination is artificial, a non-yellowing alkyd resin vehicle with pigments resistant to discoloration, such as the special types of titanium dioxide, gives good service. Aluminum paint is also used for similar purposes and especially on boiler fronts. For boiler front work, aluminum paste or powder is mixed with a vehicle having a low solids percentage and a slow-evaporating thinner. Several types of heat-reactive and air-drying finishes have been tested as protective coatings for the interior of cargo tanks containing crude oil, gasoline, fuel oil, and other refined petroleum products. At the present time, however, practically no use is being made of such coatings because none has been found satisfactory from an economical or application standpoint. There is, however, a great need for such a coating, and it is probably only a matter of time before a suitable one is developed.

#### APPLICATION

Marine finishes may be applied by either brush or spray application. In the larger and more up-to-date shipyards, spray application is probably more generally used, especially for the application of paints to the exterior surfaces. However, there is no hard and fast rule, and the method of application depends, to a large extent, on the personal opinion of the person in charge of painting. Probably the greater portion of the interior painting, such as staterooms, officers' quarters, crew's quarters, galleys, mess rooms, boiler rooms, and engine rooms, is by brush. For small pleasure craft, brush application is the principal method used.

#### CONCLUSION

The future marine finishes will follow the natural trend of developments for the paint industry. The recent use of alkyd resins is rapidly expanding, and there is little doubt that this type of vehicle will replace many of the older types of marine vehicles. Bottom paints for a long time have attracted the attention of the formulators of marine finishes and offer a field of extensive and varied research on anti-fouling agents, with special emphasis on cheaper organic materials to replace the strategic and expensive mercury compounds now



in use. Anti-corrosive paints also occupy an important place in the studies of the marine formulators. In the formulation discussions, it was felt advisable not to attempt to give specific formulations but to indicate the requirements of the different types of paint and to show how these requirements could be met through the use of the proper pigments and vehicles. The matter of selection of the proper pigments and vehicles has been left to the ingenuity and desires of the individual formulator, allowing him to formulate various products as dictated by previous experience and tests.

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## CHAPTER 12B

### FOULING ORGANISMS ON PAINTS IN SALT WATER

WILLIAM F. CLAPP

Published records of the effect of marine macro-organisms on metals and protective coatings are contradictory. In some, marine growth has been recorded as having provided protection to the material beneath; in others, definite deterioration has been attributed to the presence of marine growth.

#### Definition of Fouling Organisms

On any object submerged in salt water, organisms will eventually appear, even though they may not survive. A list of the number of species which might be found on submerged materials would include practically all the flora and invertebrate fauna present. If such organisms as *Mya* (clams), *Nudibranchiata* (sea slugs), and *Nereis* (clam worms) are listed as "fouling," it follows that practically any marine invertebrate might be included, because the organisms mentioned are only optionally present. A list of all organisms which might be found on the bottom of vessels in salt water would therefore be of no practical value.

It would seem that the term "fouling organisms," when applied to marine growth, should be restricted to those species which are capable of forming a more or less secure attachment or may contribute a more or less adherent deposit to a material.

#### Systematic Table of Fouling Organisms

Most authorities agree that the first to find attachment are the marine bacteria. In any event, all marine organisms which might be considered as fouling, in other words, all organisms which might be found on any material submerged in salt water, can be divided into one or the other of two large distinct groups.

**Group 1.** The unicellular micro-organisms composed of many species of bacteria and other plant life, and various types of Protozoa.

**Group 2.** The macro- or multicellular organisms, both plant and animal.

These groups might be further divided as follows:

1. Microbiological (unicellular, film-forming).
  1. Bacteria.
  2. Fungi.
  3. Diatoms.
  4. Protozoa (Vorticella, Suctoria, Foraminifera, etc.).
2. Macrobiological (multicellular, encrusting or fouling).
  - A. Sessile.
    1. Porifera (sponges, calcareous or siliceous).
    2. Coelenterata (Tubularia, Bougainvillia, Campanularia, and many other genera, and the calcareous corals).
    3. Bryozoa (Bugula, Electra, etc.).
    4. Annelids (Serpulidae).
    5. Arthropoda (Cirrepedia [barnacles], etc.).
    6. Mollusca (Ostrea [oysters], Anomia, Chama, Vermetus, and many others).
    7. Chordata (Botryllus, Molgula, etc.).
    8. Algae (Polysiphonia, Ceramium, Ulva, Fucus, and many others).
  - B. Semi- or optionally motile.
    1. Coelenterata (Metridium [sea anemones] and other allied genera).
    2. Annelids (worms).
    3. Arthropoda (Corophium and other Crustacea which form temporary protective tubes).
    4. Mollusca (Mytilus, Modiola, and others with holdfasts of chitinous hairs).
    5. Echinodermata (Asterias [starfish], etc.).
  - C. Motile but contributing some additional material, such as mucus, to the film over which they pass.
    1. Annelida (Polychaeta and other free-swimming worms).
    2. Arthropoda (Cancer [crabs], and many other genera).
    3. Mollusca (Nudibranchiata [sea slugs], and many genera of Gasteropoda [snails] and Pelecypoda [clams]).
    4. Echinodermata (Ophiuræ [brittle stars], etc.).

This tabulation is by no means complete, including only some of the more common organisms which have been recorded as either pro-

viding protection or accelerating deterioration on various metals or protective coatings submerged in salt water.

In addition, the list is restricted to the forms found in the temperate waters of the North Atlantic and does not include the much greater number of genera and species abundant in the more tropical waters of the Caribbean or other parts of the world. Descriptions and figures of most of the organisms mentioned may be found in standard textbooks on biology (4).

### Film-Forming Organisms

The microbiological film-forming organisms appear quickly on almost any materials submerged in salt water. In fact, most species of film-forming bacteria do not thrive or multiply rapidly until they do become attached to some base. Many observations indicate that the multicellular, fouling organisms rarely secure a firm foothold on any surface until after the formation of an organic film. The point of attachment for the larger organisms may therefore be said to be not in direct contact with a material but separated by a film which is to some extent organic. In order to understand the effect of the various species of macro-organisms on different materials, some knowledge of the nature of the organic film is necessary, since the firmness of attachment of the larger organisms must depend to some extent upon the adhesion of the organic film. The major portion of this film is made up of numerous forms of bacteria, but some fungi, molds, diatoms, and protozoans are also generally present. Most of the bacterial portion of the film is composed of colonies formed from single individuals which have become securely fastened to the surface, rather than by the addition of later arrivals.

In normal salt water, the surface of most materials may be completely covered with a microbiological film in a very few hours. Scores of different forms of film-forming bacteria are known, but not all marine bacteria are film-forming.

Zobell found that on glass slides approximately one-third of the species of bacteria present in the sea water became firmly attached to the surface of the glass. He also believed that firm attachment of a bacterium is not immediate, the cementing process requiring several minutes.

The nature of the attachment of the bacterial colonies is not thoroughly understood, but some appear to excrete or exude a film of gelatinous or mucilaginous material which soon hardens and in which they

are then partially embedded. Even on polished glass, swiftly running water will not remove this film once it is formed.

In addition, certain forms of denitrifying bacteria are known to precipitate calcium carbonate from sea water (9, p. 4; 1). This may account for at least some portion of the very adherent calcium carbonate coatings found on metals submerged in salt water, occasionally even on the very high copper alloys.

Sulfate-reducing bacteria are also plentiful in some microbiological films. Haase (2), however, records a very great deal of hydrogen sulfide in films where no trace of sulfate-reducing bacteria could be found and infers that the sulfur must have originated from Algae.

Iron bacteria commonly found in microbiological films do not appear to directly affect ferrous metals but do precipitate iron which is already in solution. The addition of this precipitate to the film may affect the rate of deterioration. Certain bacteria are also believed to be responsible for deposits of silica occasionally found on ferrous metals.

There is a considerable variation in the numbers of film-forming organisms present at different locations. This may be due to some forms of pollution, to differences in salinity, or to other local factors.

There is also a very marked seasonal variation in the number of film-forming organisms at a given location, temperature being the most important factor governing this variation.

### Composite Films

The microbiological film on metals cannot always be considered as composed entirely, or even mostly, of the organisms originally responsible for the film. Turbid waters containing more or less microscopic organic and inorganic material in suspension may deposit some portion of this material upon a microbiological film, thus building a composite film of a structure very different in nature from the original purely biological film. Additional living micro-organisms may form a new film over this microscopic detritus. In comparatively thick films, the organisms in the earlier layers may die and the product of this decay may be corrosive or injurious.

Corrosion products may also contribute to and affect the film in several ways. Heavy deposits of a more or less adherent corrosion product may result in the death of the micro-organisms. This is particularly true with iron and mild steel since in these metals the corrosion product appears as quickly as the organic film. In copper the

corrosion product is not adherent. It is therefore possible that the corrosion of copper or the high copper alloys may affect the microbiological film by providing a very insecure non-adherent base for attachment, as well as providing a condition highly toxic to some of the organisms.

### Physical Nature of Surface

The condition or nature of an exposed surface affects the firmness or permanence of attachment of an organic film. Even on polished glass, a very adherent continuous microbiological film of measurable thickness may be built up in twenty-four hours.

Different metals, alloys, and protective coatings offer very different surfaces for the attachment of the film-forming organisms. Most of the irons and mild steels do not provide an even smooth surface when compared with the various stainless steels, copper alloys, Monel, aluminum, etc. It can be seen that many factors may affect the microbiological film on metal or protective coatings.

A smooth surface of hard rubber is generally subject to less fouling than that of soft rubber. This may be a matter of poor adhesion rather than a question of any effective difference in toxicity in the two materials.

A complete biological film may be considered as protective, but, if broken or incomplete, accelerated corrosion may be expected where a metal is more or less exposed, similar to the effect produced by failures in protective coatings (5, p. 10).

### Multicellular Fouling Organisms

It is known that, on some surfaces, certain encrusting organisms are protective. It is also certain that many of the encrusting and fouling organisms accelerate deterioration. The accumulation of data in recent years indicates that organisms play a very important part not only in their effect on metals but also in their effect on protective coatings.

Many theories have been offered to explain the deteriorating effect of the various encrusting macro-organisms. Some may be enumerated as follows:

1. That some secrete an acid or a corrosive fluid.
2. That the powerful digestive fluids of the stomach and alimentary canal of some marine invertebrates may accelerate deterioration.

3. That, although the living organisms may be protective, the products of decaying animal matter may cause excessive deterioration.

4. That the encrusting organisms may form semi-permeable bases which favor the development of concentration cells, resulting in corrosion either directly beneath or around the periphery of the base of the organisms, depending on the type of concentration cell that develops.

### **The Effect of Color**

It should also be mentioned that the embryos of many fouling organisms are affected by light and that marine growth on dark surfaces is always much heavier than on light surfaces (6, 7).

In studying the effect of the larger multicellular marine organisms on materials in salt water, it is necessary to take into consideration the nature of the base to which they become attached—whether it is a biological film or a composite film of both organic and inorganic material.

### **Attachment of Embryos**

Rarely do the embryos of multicellular marine organisms become attached to a submerged material until some film is formed. All fouling and encrusting macro-organisms become attached as microscopic embryos. This is true both of plants and animals. In many cases the embryos of these organisms are free-swimming. They have little choice, however, in the selection of the material they land upon. If it is unfavorable, they generally die. The young of *Balanus* have been observed moving for a short distance over a surface in an effort to secure a favorable firm attachment. But the embryos of most fouling species must attempt to secure a firm foothold on a material, wherever they may happen to land on it. The somewhat gelatinous sticky surface of the microbiological film supplies a much more satisfactory material for this purpose than would a clean, bare metal or hard protective coating. Upon the nature of this film depends the firmness of attachment of the embryos of the larger organisms.

### **Encrusting Organisms**

Authorities are in complete disagreement in their opinions regarding the effect of some encrusting organisms such as the various species belonging to the genus *Balanus* (certain barnacles). In published reports, these organisms are stated to have provided protection as frequently as they are accused of causing corrosion. Recent observations

indicate that, because of very important structural differences, some of the scores of species of *Balanus* may provide protection whereas others cause corrosion. Furthermore, it appears that the effect of a given species of *Balanus* may vary on different materials. But this effect again may be influenced by the type of microbiological film which provides support for the larger organisms.

*Balanus eburneus* and many other related species build a more or less solid base of calcium carbonate, frequently a millimeter or more in thickness, completely insulating the body of the animal from the metal beneath.

In other species of barnacles, this base is more or less porous, and *Balanus balanoides*, *Chthalamus stellatus*, and many other species do not provide themselves with this protective base. For this reason, *Balanus eburneus* provides more or less protection to some materials, whereas *Balanus balanoides* may accelerate deterioration.

Many encrusting organisms such as *Ostrea* (oysters) and *Balanus eburneus* may appear consistently to provide some protection against deterioration on a certain material. But these and many other organisms grow very rapidly under favorable conditions. Weaker organisms or later arrivals are frequently covered and killed by more rapidly growing neighbors. Decay resulting in the formation of sulfur compounds may accelerate deterioration; the failure of a protective coating and a normally protective organism may become indirectly responsible for the corrosion of a metal or the deterioration of a paint film.

Many of the fouling organisms have a comparatively brief span of life. During the course of a year many individuals, one after another, fasten to a certain spot as embryos, grow to maturity, and die. Some fall off but many of the dead remain entangled in the encrusting material and are in turn buried by later arrivals.

In addition to the possible destructive or protective effect of a given organism on a metal surface, many of the organisms listed are capable of causing serious damage to various types of protective coatings. Failure of such coatings may be due to the direct contact of decomposing organic matter in the encrusting film with the paint system. But failure due to encrusting organisms is frequently caused by the mechanical strain on the paint system by the growing organism. This is particularly true with most species of *Balanus*. The embryonic *Balanus* starts adult life by excreting a minute calcium carbonate base, which it firmly attaches to the surface upon which it rests. As it grows, this base is rapidly enlarged, horizontally. In constructing the base it is evident that there is considerable mechanical downward pressure exerted as well as horizontal, to the extent that the organism



when fully grown is embedded to a greater or lesser extent in the paint surface. In the case of some heavy bitumastic coatings, *Balanus* have by this means, while growing, gradually forced the base completely through  $\frac{1}{8}$  inch or more of the coating in such a manner that the entire outer circumference of the *Balanus* base is finally forced through to a firm contact with the bare material beneath.

In such cases an examination of the underside of the barnacle base shows that it is conical rather than flat, as is normal, and that this cone is filled with the protective coating through which the organism has gradually forced its way. The effect of this mechanical strain has been observed in many types of protective coatings varying from microscopic depressions to the deep pits mentioned above. It has also been observed that this stress developed in the growth of the organism may affect a protective coating to the extent that, when the organism is removed or falls off, it carries with it the entire paint system, which is directly beneath the base, whereas, in the area surrounding the organism, the paint remains firmly attached.

### Exposure Tests

A large proportion of the published data referring to the effect of organisms on metals and protective coatings has been based on observations made at infrequent intervals at testing stations where test panels have been exposed.

After a material has been exposed for a comparatively long period of time some evidence occasionally remains which may indicate the particular organism which appeared to have originally provided protection or aggravated deterioration. Generally, however, other organisms, later arrivals, and other factors have succeeded in destroying this evidence.

In a very large majority of all salt water exposure tests which have been conducted on metals and on protective coatings, the materials have been examined and the results recorded only after comparatively long periods of exposure.

Eventually so much has happened on a submerged test panel that it is very difficult to determine which organism or what condition may have been responsible for any corrosion found on a metal, or deterioration in a protective coating. In most cases so much activity has occurred on the tests that it is only possible to record what has happened. To determine why is practically impossible. The investigator can only speculate on the probable cause. The factors are so numerous and conditions so variable that we have practically no definite data

concerning the effect of specific organisms on metals submerged in salt water.

### Future Research

To determine accurately the effect of any species of marine organisms on a particular metal or alloy, or protective coating, it would be necessary to make frequent observations from the time of exposure of the material and the attachment of the embryo, through maturity to death and disintegration. This is a comparatively short period for all but a few of the encrusting or fouling organisms. Such observations would have to be made without injuring or disturbing not only the individuals of the particular species being studied but also the microbiological film. This could be accomplished only in a biological laboratory with proper facilities to enable the investigator to control the various factors. In a laboratory equipped with batteries of tanks with a controlled flow of salt water, it would be possible not only to restrict the encrusting or fouling organisms to a single species, but the effect of each organism could be observed as frequently as necessary without affecting the normal growth and activity. It would seem that studies under these conditions would be of great value in providing more definite information in connection with deterioration due to fouling organisms and of methods and materials for providing protection.

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## CHAPTER 13

### RAILROAD COATINGS

OTTO J. MILETI

The development of surface coatings for the railroad industry has followed the progress of the paint industry. In the early days, oil finishes were used, but, later, lacquers were employed, followed progressively by quick-drying varnish type finishes and alkyds. As the paint industry developed new and better products, the railroads began to use them for the protection and decoration of their equipment.

The problem of surface protection is very important to the railroad. Paint must be applied not only for beauty and decoration but for protection as well, because all railroad equipment or "right of way" must withstand the elements for many years.\*

The application of finishes also changed with modern progress, from brushing to spraying when the air spray was introduced.

Owing to the many varieties of railroad equipment which must be coated and protected, it is necessary to classify the equipment in two groups: (1) rolling stock and (2) maintenance of way.

Rolling stock is the equipment which makes up the train and presents the problem of finishing both the interiors and the exteriors of (a) locomotives; (b) passenger cars; (c) freight cars; (d) cabooses.

Maintenance of way, in a broad sense, signifies any railway equipment not a part of the train, such as (a) passenger and freight stations; (b) roadbed and signals; (c) bridges.

Paint finishes for the interior and exterior of stations, signals, and bridges are important, from both a decorative and a protective viewpoint.

#### ROLLING STOCK

##### Locomotives

The coating of locomotives presents six different finishing problems:

1. The fire box and front end.
2. The boiler jacket, cab, cylinders, wheels, and tender.

\* Generally speaking, signals are painted every year; passenger cars every three years; bridges every five years; and freight cars every eight to ten years.

3. The interior of locomotive cab.
4. The interior of water tank.
5. The outside of boiler.
6. The coal space.

**1. The Fire Box and Front-End Paint.** This paint should have the property of withstanding heat. Since relatively high heats are attained, the paint will eventually burn and wash off. It is desirable, therefore, to have a coating that will fail uniformly at high temperatures without building up or sealing.

Many railroads coat the fire box proper by applying crude or waste oil; others use the same paint as applied on the front end; and some do not paint the fire box at all.

For front-end paint, many railroads use their waste lubricants in which they mix a varying amount of flake graphite and white lead in linseed oil. This paint is applied while the parts are hot, and, after the paint is dry, the surface is polished with waste to bring out the graphite finish. Although this finish costs very little, its life is short, and it must be renewed after almost every trip.

There are a few graphite type, front-end paints on the market that serve very well. The cost must necessarily be higher than the graphite-white lead mixture but the prepared graphite type usually lasts much longer. Although of a variable composition, it consists essentially of amorphous and flake graphite, vegetable, animal, or mineral oils or waxes, often with the addition of a small amount of white lead and aluminum powder. Some railroads use an asphalt type of paint, composed of varying amounts of gilsonite and petroleum asphalt, with or without vegetable or animal oils, thinned with kerosene and mineral spirits. This type of paint has a tendency to build up and therefore cannot be used on the fire box proper, because it may stop the telltale holes of the staybolts.

Another method of finishing front ends is to apply a coat of clear varnish. While the varnish is still tacky, graphite is sprinkled over it and then the surface is polished. This method will give the brightest finish, but its durability is poor.

**2. The Boiler Jacket, Cab, Cylinders, Wheels, and Tender.** Locomotive enamels are used in finishing the outside of the locomotive and tender, the boiler jacket, cylinders, wheels, and cab. These parts are first primed with an iron oxide quick-drying varnish type primer followed by two coats of enamel. A typical railroad specification is:

## LOCOMOTIVE BLACK FINISHING VARNISH

<i>Pigment</i>	5% Maximum
<i>Liquid</i>	95% Minimum
<i>Pigment</i> : Shall be pure carbon black of a blackness equal to railroad standard.	
<i>Liquid</i> : Spar varnish, 90% minimum; drier and thinner, 10% maximum.	

The physical properties and tests are then listed by the specifications, which vary with the different railroad requirements.

In the specification under discussion the requirements for the liquid portion are incomplete in that neither the nature nor the percentage of the non-volatile is definitely indicated.

A better way of specifying the liquid is to require that the spar varnish meet Federal Specification TT-V-121a. This insures an excellent, durable type of varnish that meets the most rigid demands of any railroad.

If the locomotive is to be painted any other color than black, the proper quantity of colored pigment is used in place of carbon black, and any necessary volatile adjustment is made.

Within the past few years, the alkyd types of finishes have come to the fore. These enamels possess better color and gloss retention on exposure than the oleoresinous group. The alkyd type best suited for locomotive finishing is the long-oil type with slow-evaporating solvents which permit ease of brushing and dry through hard overnight.

Lacquer is still used for locomotives by some railroads, but its use is rapidly diminishing. Lacquer possesses good durability and would be used more extensively if the original cost were not higher than the enamel finish.

**3. Interior locomotive cab enamel** is usually of a light green shade. A finish of this type should dry hard and elastic and possess resistance to repeated washings with mild cleansing solutions. A vehicle suitable for an enamel of this kind is a spar varnish, such as Federal Specification TT-V-121 or TT-V-121a.

**4. The interior of the water tank** is usually coated with red lead. A very good grade is formulated as follows:

235	lb.	red lead (95% $Pb_3O_4$ ).
25½	lb.	litharge ( $PbO$ ).
6½	gal.	linseed oil.
¼	gal.	turpentine and drier.

A paint so formulated does not possess good storage properties for it thickens and eventually hardens in the container because of the reaction between the litharge and the linseed oil. For this reason such a product must be made immediately before it is used. If the paint is to be kept in storage for any length of time, the litharge should be added just prior to the application of the paint. Two coats are ordinarily applied, and to eliminate the possibility of skip spots the top or second coat is tinted with a small amount of lampblack to give a contrast between coats.

There are other finishes on the market superior to the red-lead, linseed oil type, such as the iron oxide-zinc chromate phenolic varnish primer which is finding a ready market.

The inside of the tender tanks, as a rule, are not painted because the boiler feed-water is sometimes treated with soda ash, which is quite destructive to ordinary paint films.

**5. The Outside of the Boiler.** It has been customary to paint the outside of the boiler with red lead or iron oxide paint before applying the insulating material and the jacket. In the past few years, however, considerable interest has been shown in a heat-resisting aluminum paint.

**6. The Coal Space.** The tender part, used to store coal, is usually coated with an iron oxide or iron oxide-zinc chromate paint, although some roads use a petroleum product containing a soluble chromate rust inhibitor.

### Passenger Car Finishing

Passenger car finishing has followed very closely the development of the new types of automobile finishes, although the railroads have lagged in adopting the newer products. Here, too, decoration and protection of the interior, as well as the exterior, of the car are essential. There are four distinct types of finishing systems: (1) color varnish; (2) lacquer; (3) synthetic finish, including (A) phenolic varnish and (B) alkyd varnish.

**1. Color Varnish \* System.** A typical system for finishing coaches, requiring about eight days, was developed in accordance with the following typical scheme:

\* Color varnish is really a highly pigmented enamel. It contains as much pigment as the clear varnish will carry and, as a result, yields a fuller film than the normal enamel. Because of its high pigmentation, color varnish dries more thoroughly and has better sanding characteristics than normal enamel. It will not weather so well as enamels and, therefore, is usually varnished.

One coat of iron oxide varnish base primer. Dry overnight.

One coat of gray surfacer. Dry overnight.

Spot-putty and knife with knifing compound. Dry overnight.

Rub with rubbing stone or pumice and water. Dry overnight.

Two coats of flat or semi-gloss olive-green \* colored varnish. Dry overnight between coats.

Two coats of clear finishing varnish. Forty-eight hour dry between coats.

Each coat is permitted to air-dry overnight, then sanded before the next coat is applied. Before the clear finish is applied, a day is usually required for lettering the car. This lettering is air-dried overnight and varnished the following day. Forty-eight hours' drying should be allowed before the second coat of varnish is applied. This system is still used by some roads today, and the durability is dependent on the quality and type of varnish used.

Some roads use enamel in place of the flat or semi-gloss color varnish and do not apply finishing varnish until the enamel has lost its gloss. This dulling develops within a period of six to eight months. Other roads use two coats of gloss enamel and do not re-coat with finishing varnish.

Of historical interest, a finishing system for passenger cars of wood or steel construction, used as late as 1927, and requiring twenty-one days to complete, follows:

- |                     |  |
|---------------------|--|
| <i>First day:</i>   | Sand-blast and prime.  |
| <i>Second day:</i>  | Straighten metal and touch up spots with a mixture of one-half primer and one-half surfacer by volume. |
| <i>Third day:</i>   | Apply first coat of surfacer.  |
| <i>Fourth day</i>   |  |
| <i>Fifth day</i>    | Apply additional coats of surfacer each day,   |
| <i>Sixth day</i>    | sanding between coats.   |
| <i>Seventh day:</i> | Spot-putty and knife.  |
| <i>Eighth day:</i>  | Apply a guide coat † and water-rub.  |

\* Known as Pullman Green. Some railroads use maroon (Tuscan), blue, green, etc.

† The guide coat is prepared by mixing ocher with turpentine and then adding a small amount of varnish as binder. This coat is applied over the knifing coat to guide the "rubber" and to insure that the surface is properly rubbed.

- Ninth day:* Apply first coat of colored varnish.  
*Tenth day:* Apply second coat of colored varnish.  
*Eleventh day:* Letter.  
*Twelfth day:* Apply first coat of finishing clear varnish.  
*Fifteenth day:* Apply second coat of finishing clear varnish.  
*Eighteenth day:* Apply third coat of finishing clear varnish.  
*Twenty-first day:* Release cars.

**2. Lacquer System.** This type of system was adopted about 1926 by some railroads and is still extensively used. Lacquer gives a satisfactory finish on steel cars but has poor durability on wood.

Lacquer systems generally use the oil type of primer and surfacer as in the varnish system, the lacquer products being only the last two materials: sealer coat and colored lacquer.

A typical system is:

One coat oil-base lacquer primer.

One coat oil-base lacquer surfacer.

Spot-putty and knife. Permit to air-dry overnight.

Rub with rubbing stone or pumice and water.

Apply one coat lacquer sealer. Permit to air-dry 2 to 4 hours and then apply first coat of colored lacquer.

Follow with two or three coats of colored lacquer.

The sealer coat is applied after the rubbing operation to act as a sort of sealer to minimize the danger of lifting the oil type undercoats by the colored lacquer coats.

The gold leaf or imitation gold lettering is protected by a finishing varnish or clear lacquer.

The same procedure is used in finishing the interior and the exterior of the car, except that for the interior primer and surfacer are generally very light colored.

**3. Synthetic Type Finishes.** There are two distinct materials suitable for both brush and spray applications. One material is either the phenolic or modified phenolic type; the other is the alkyd type.

*A. The Phenolic Finishes.* These finishes were introduced before the alkyds. A typical system is:

One coat primer.

One coat surfacer.

Spot-putty and knife.



Water-rub (rubbing stone and water).

Two coats of color varnish flat.

One or two coats of clear finishing varnish.

Each coat air-dried overnight before the following coat is applied.

This same system can be used on the interior, with gloss enamels in place of the flat color varnish, omitting the clear finishing coat.

As an interior finish, the phenolic type yields excellent results because the coat is hard and elastic and possesses good washability.

This system, exterior or interior, generally makes use of the older type of oil primer and surfacer, but sometimes the phenolic types are employed. It is advisable to use a modified phenolic resin varnish in the formulation of phenolic types of primers and surfacers. A good recommendation is at least a 50 per cent modification of the phenolic resin, with ester gum or Congo resin as the modifying resins. The oil should be a minimum of 25 per cent linseed with remainder tung oil. Phenolic types of primers made with straight unmodified phenolic resins and all tung oil result in a hard non-porous film which, when recoated, will lack adhesion.

*B. The Alkyd Varnish Finishes.* These finishes may be applied by spray or by brush. A typical system is:

One coat of primer.

One coat of surfacer.

Spot-putty and knife.

Water-rub.

Two coats of gloss enamel.

All coats are permitted to air-dry overnight before succeeding coats are applied.

This system is good for the interior as well as the exterior of the car. Sometimes for exterior use it is followed with one or two coats of clear alkyd varnish. Also it is the practice of some railroads to add clear varnish to the last enamel coat for better gloss and fullness.

If no clear varnish coat has been applied, the lettering has to be protected separately with a clear varnish. Some roads are using the imitation gold alkyd enamels for lettering without any protective clear topcoat and are getting good results.

### **Freight Car Finishing**

The report on railroad equipment of June 30, 1938, gives the following statistics:

43,119 steam locomotives.

756 electric locomotives.

297 internal combustion locomotives.

45,659 passenger cars, of which

7,726 are owned by the Pullman Company.

2,699 are self-powered passenger cars (motor cars).

1,708,030 freight cars.

(About) 300,000 freight cars owned by private companies.

(About) 75,000 railway service cars.

It can readily be seen that the greatest need for protective coating is in the freight car field. The various classes of freight cars are:

Box cars.

Gondola and hopper cars.

Stock cars.

Flat cars.

Refrigerator cars.

Tank cars.

In considering finishes for freight cars, some thought must be given to the various types of exposure which these finishes must withstand. For instance, the finish applied to the underframe and running gear is subjected to moisture as well as considerable abrasion from flying particles stirred up by the velocity of the train. However, it has little exposure to sunlight. The finish used on the roof and sides receives abrasion from cinders as well as the direct effect of weathering, including sun and rain. Finishes used on the inside of freight cars are subjected to the mechanical action of the lading, as with coal, and possibly to chemical action from cargoes of lime, soda, or fertilizer. With these in mind, finishes should be selected which will best withstand the type of haul intended for the car, the location of the road, and the climate.

**Box Car Finishing.** There are two types of box cars: the wooden side car and the more recent steel car.

*Wood Cars.* In painting the wood car, it has been customary to use three coats of iron oxide paint. The first coat is usually similar to the second and third coats, except for pigment content, which is 32 to 35 per cent for the first coat and 40 to 45 per cent for the other two coats.

A typical formulation for this system is:

## RAILROAD COATINGS

## FIRST COAT

Ferric oxide ( $\text{Fe}_2\text{O}_3$ )	18.5%
Extender pigments	15.5%
Linseed oil	38.0%
Thinning mixture	28.0%
	<hr/>
	100.0%

## SECOND AND THIRD COATS

Ferric oxide	24.0%
Extender pigments	20.0%
Linseed oil	32.0%
Thinning mixture	24.0%
	<hr/>
	100.0%

The linseed may be either raw or boiled, and the thinning mixture should contain at least 40 per cent non-volatile base.

*Steel Cars.* The following system is used in painting steel cars:

One coat primer.

Two coats iron oxide paint for red cars

or

Two coats black oil paint for black cars.

If red lead is used for priming, it should be air-dried for at least two days before the red or black paint is applied. The two coats of paint are applied one day apart.

*Primer.* There are three different types of primers in major use:

Pure red lead primer.

Extended red lead primer.

Iron oxide-zinc chromate primer, also called anti-corrosive primer or zinc chromate primer.

*Red lead paint.* A typical pure red lead primer specification reads as follows:

Red lead (95% $\text{Pb}_3\text{O}_4$ )	100	lb.
Raw linseed oil	27½	lb.
Drier and volatile thinners	3½	lb.

*Extended red lead primer.* Although extended red lead primer will not give quite the protection of a pure red lead paint, it is more fool-proof from the standpoint of crawling of finishing coats and has less tendency to settle hard. It is more economical than straight red lead.

A typical specification is:

FOR BRUSHING

Red lead (95% $Pb_3O_4$ )	55.0%
Extender pigments	18.0%
Raw linseed oil	19.5%
Drier and volatile thinners	7.5%
	100.0%

FOR SPRAYING

Red lead	52.5%
Extender pigments	17.5%
Raw linseed oil	18.5%
Drier and volatile thinners	11.5%
	100.0%

The specification for brushing is given because this primer is used between metal joints and all other parts which would be concealed after the car is built. It has been found that an addition of 10 to 25 per cent of neutral spar varnish will help the drying of this primer, and that successive coats of paint will have better adhesion. The addition of 5 to 10 per cent of the recently introduced metallic lead pigment has been found helpful in preventing crawling.

*Anti-corrosive primers* of the iron oxide-zinc chromate type have come on the market only in the past few years. A typical specification is:

Iron oxide pigment	23.0%
Zinc chromate	11.5%
Extender pigment	11.5%
100% phenolic varnish *	54.0%
	100.0%

\* The 100% phenolic varnish employed is 25 to 50 gallons in length and contains 50% non-volatile.

This type of primer dries faster and harder, has better adhesion, and the top coat of paint will not crawl.

Some roads use an iron oxide primer, and, lately, others have used a clear unpigmented primer containing soluble chromates as a rust inhibitor. All these primers will air-dry permitting recoating the following day.

*Iron oxide paint.* The two coats of paint applied over the primer are usually of the same specification as that used for wooden cars.

Of course there are times when no special primer is used on a steel car. Then, two or three coats of the same paint are applied. The primer coat should contain some tung oil varnish (10 to 25 per cent of the vehicle) on the order of Federal Specification TT-V-121a. This will give better through drying and better moisture resistance. This will also be true if only two coats of paint are applied.

Coal cars and other cars that are finished in black use the same primers that are used on steel cars. A typical black paint for second and third coats is composed of:

Carbon black (or lampblack) . . .	6.0%
Red lead . . . . .	2.0%
Extender pigments . . . . .	20.0%
Raw linseed oil . . . . .	43.0%
Drier and volatile thinners . . . .	29.0%

100.0%

*Quick-drying and synthetic paints.* The foregoing paragraphs describe only the old type of straight oil finishes that have been used on freight cars for many years. In the last decade, the *quick-drying* type as well as the synthetic type of protective coating was introduced.

*Quick-drying \* freight car paint.* This type of paint will allow, under favorable working conditions, the application of two coats (two-a-day system) and stenciling the car on the same day.

This kind of paint contains the same general type of pigment as the oil paint but usually in lesser quantities. The vehicle is composed of treated bodied oils of different types and volatile thinners, with or without the addition of resins.

If this paint is properly formulated, it will have unusually good durability. Best results are obtained if the primer is hard-drying, the preference being for an iron oxide-zinc chromate primer described previously.

*Freight Car Synthetic Finishes.* This type of protective coating is being used in limited amounts because of its original high cost. Oil-modified alkyds of over 50 per cent oil content are generally used as a vehicle with or without the addition of vegetable drying oils.

If properly formulated, this is probably the best finish for the freight car. It is recommended that only one coat a day be applied and that a good anti-corrosive, hard-drying primer be used.

\* This type of paint, which is used extensively today, is generally recoated in 45 minutes to 4 hours. Much care must be given to its formulation, so that it will not wrinkle, blister, or sag.

Maximum durability is unimportant to the railroads because repairs are generally needed in approximately five years. The color retention, film integrity, and hardness are superior qualities of this type of finish. Therefore with these finishes the cars will look much better while in service.

A typical specification is:

#### SECOND AND THIRD COATS

Iron oxide ( $\text{Fe}_2\text{O}_3$ )	13.5%
Extender pigment	11.0%
Alkyd resin	40.5%
(Solid 60% oil-modified)	
Volatile thinners	35.0%
	<hr/>
	100.0%

#### SOLUBLE NAPHTHENATE DRIER

0.6% Lead	Based on the
	non-volatile
0.06% Cobalt	of liquid

*Semi-paste Paints.* A large quantity of semi-paste paints is used in finishing freight cars. These pastes are reduced for use with various amounts of thinning oils. A few freight car pastes and thinning mixtures are:

#### OXIDE OF IRON SEMI-PASTE

Pigment	70.0%
Linseed oil	30.0%
	<hr/>
	100.0%

#### *Pigment:*

Ferric oxide ( $\text{Fe}_2\text{O}_3$ )	50.0% min.
Silica, China clay, asbestine, or a mixture thereof	Remainder

This particular paste can be reduced by adding to one volume of paste one and one-half volumes of boiled linseed oil, or one and one-half volumes of thinning mixture. Mixtures of boiled linseed oil and thinning mixture can be used. These will give a very satisfactory freight car paint.

#### BLACK SEMI-PASTE PAINT

Pigment	50.0%
Linseed oil	50.0%
	<hr/>
	100.0%

*Pigment:*

Lampblack or carbon black	20.0% min.
Red lead	5.0% min.
Silica, China clay, magnesium silicate, or a mixture thereof	75.0% max.
	<hr/> 100.0%

This paste can be reduced in the same ratio as the iron oxide paste, namely, 1 to 1½ volumes.

*Thinning Mixture or Paint-Thinning Oils.* In a majority of instances the semi-pastes are thinned with a straight thinning oil, though straight boiled linseed may be used. They are also reduced with equal parts of boiled linseed and thinning oil.

Below is a typical specification for a thinning oil:

## THINNING MIXTURE FOR PAINT

Drier and resins	10.0% max.
Fixed oils	40.0% min.
Mineral spirits	50.0% max.
	<hr/> 100.0%

The drier may be of the oleate, linoleate, or resinate type.

The resins shall consist of fused fossil gums or rosin which has been partially neutralized with glycerol or hydrated lime. In most instances, the resin used is rosin because this is the cheapest and most suitable for the purpose.

The fixed oils shall contain at least 60 per cent of linseed, the rest being other drying or semi-drying oils.

This type of thinning mixture is used when a semi-paste is reduced only with straight thinning mixture.

If the reduction is with equal volumes of boiled or raw linseed oil and thinning mixture, the percentage of non-volatile in the thinning mixture is usually reduced to 35 or 40.

Gondola, hopper, stock, and flat cars are usually finished with one of the systems previously mentioned for box cars.

**Refrigerator Car Finishing.** On a refrigerator car, the exterior, the roof, ends, and trucks are generally finished with the same material as the box car. The sides are usually painted yellow or orange or some other light color. The finishing material is mostly of the enamel type. A typical specification is:

## FIRST COAT

Pigment .....	33.4%
Vehicle .....	66.6%
<hr/>	
100.0%	

*Pigment:*

Chrome yellow .....	50.0%
White lead .....	30.0%
Silicates .....	20.0%

*Vehicle:*

Linseed oil .....	43.6%
Tung oil .....	17.4%
Lead and manganese driers .....	0.4%
Volatile thinners .....	38.6%

100.0%

100.0%

## SECOND COAT

Pigment .....	41.0%
Vehicle .....	59.0%
<hr/>	
100.0%	

*Pigment:*

Chrome yellow .....	43.3%
White lead .....	32.4%
Silicates .....	24.3%

*Vehicle:*

Synthetic resin .....	11.5%
Linseed oil .....	15.2%
Tung oil .....	14.0%
Lead and manganese driers .....	0.3%
Volatile thinners .....	59.0%

100.0%

100.0%

## THIRD COAT

Pigment .....	30.0%
Vehicle .....	70.0%

100.0%

*Pigment:*

Chrome yellow .....	61.6%
White lead .....	19.2%
Zinc oxide .....	19.2%

*Vehicle:*

Synthetic resin .....	14.0 %
Linseed oil .....	18.5 %
Tung oil .....	17.13%
Lead and manganese driers .....	0.37%
Volatile thinners .....	50.0 %

100.0%

100.0%

The vehicles used in both the first and second coats are processed. The vehicle in the third coat is the same as that in the second, but with 50 per cent volatile thinners. The synthetic resin, in this instance, may be a modified or a pure phenolic resin. The pigment may be



straight lead chromate meeting certain railroad color standards or a mixture of lead chromate, white lead, and zinc oxide.

Another satisfactory finish for refrigerator cars is the alkyd type. This finish, while not so water- and brineproof as the phenolic type, is satisfactory and has good color and gloss retention.

Some railroads still use the same type of oil paints that are used in painting box cars, except that the pigment is yellow or orange lead chromate instead of iron oxide. The top or third coat is usually made without extender materials and with the addition of some varnish.

If the refrigerator car is made of steel, the best first coat would be the anti-corrosive primer previously described.

*Interior Finishing of a Refrigerator Car.* The interior of a refrigerator car is generally finished with a clear varnish. Any water-resisting spar varnish will be suitable. Federal Specification TT-V-121 or TT-V-121a gives a satisfactory finish.

Some refrigerator cars are painted light gray with a good grade of spar (water-resistant) interior enamel.

If an aluminum finish is desired, preference is for the phenolic type of aluminum vehicle.

In some cases, an odorless finish is required in which a well-plasticized lacquer enamel of the desired color is used.

**Tank Car Finishing.** Tank cars are used for transporting many different liquids requiring exterior finish to withstand certain specific materials.

The tanks used to transport chemicals represent an individual problem, but the bulk of tanks are finished with:

One coat of primer and

Two coats of black paint in most instances, enamel.

If a black oil paint is to be used, a red lead primer is satisfactory. If a black enamel is to be used, the primer must be hard drying. The anti-corrosive primer mentioned previously is highly satisfactory. The black paint could be any of those used for box cars (oil, quick-drying, synthetic). The black enamel could be any one of those specified for locomotive finishes.

The painting of the interior of tank cars that are used to ship strong chemicals has recently been thoroughly investigated. New types of resins, such as chlorinated rubber, have made available coatings to resist certain chemicals, and time will ultimately demonstrate their usefulness and durability.

### **Caboose Finishing**

Several of the railroads finish the caboose with a bright red enamel or paint; others use the same oxide paint as on the box car. If a bright red is required, it is preferable to specify toluidine toner. This pigment, with or without extender, will retain brightness much longer than other commonly used red organic pigments, such as para or lithol toner.

Since the caboose should be seen even under conditions of poor visibility, efforts should be made to formulate a paint or enamel of good gloss and color retention. This has been accomplished with the alkyd type finishes. If an enamel finish is desired, the same type of alkyd resin used for passenger car finishing should be employed. If a paint is preferred, the resin used in freight car paint formulation should be employed.

The interior of the caboose is usually painted with a green flat or semi-gloss wall paint. The lower section is generally painted a darker shade than the upper section of the wall and the ceiling.

**Spot Sealer.** This type of paint is used to cover greasy and dirty spots in the interior of a box car and thereby make it suitable for the transportation of grains, flour, and other edible products. It is a quick-drying paint, usually made of pigment ground in pure orange shellac or in shellac substitute made from Manila, loba, or pontianak resins. It must dry hard over grease and oil and must seal them.

The success of this type of finish, called "box car floor sealer," is due to the proper preparation of the floor. Splinters that stick up from the floor often act as wicks to draw up the oil through the sealer film and stain the lading. Wire brushing will remove these objectionable splinters. Singeing with a torch makes the splinters more brittle, therefore more easily removed. It is considered advisable also to remove as much grease or oil as possible from the floor by wiping with waste or rags before the application of the floor sealer.

This same sealer is sometimes used to block out old stenciling on a freight car because it will allow restenciling almost immediately.

**Truck Finishing.** The trucks of freight cars are usually finished with one coat of primer followed by either one or two coats of black or red paint. These paints are the same as those used on the body of the car.

The trucks are sometimes finished with one coat of asphaltum asbestos paint over a primer. The same paint, called car cement, is used

on ends, doors, and roofs of box cars. This car cement is effective only if a good primer is used under it, because the film is porous and the lack of primer may cause rusting of the metal.

**Stencil Paint.** This paint is generally used in semi-paste form because most of the stenciling is done with a brush. The soft semi-paste white lead (89 per cent lead, 9 per cent linseed oil, 2 per cent turpentine) has proved most satisfactory.

Lately, some lettering has been done with aluminum, by the stenciling brush method. The use of aluminum stenciling should grow because it has good durability and good visibility if properly formulated.

## MAINTENANCE OF WAY

### Station Paints

For both the exterior and interior of depots and other railroad buildings, the same type paint is used that is recommended for houses. On the exterior, the preference is for the lead type of oil paints with or without zinc oxide and extender, although much lithopone and titanium pigments are used by some roads. On the interior, standard wall paints and interior trim enamels and floor enamels are used. First-grade material will meet the requirements of any railroad for this type of finish.

### Signals

Protective materials for signals are given considerable thought by the railroads for here color retention is paramount. Efforts should be made by the railroads to standardize the shades of red, green, and yellow which are used.

Some railroads prefer oil paints, others enamel. The enamel type of finish is more satisfactory, especially if it is formulated to obtain a maximum of color and gloss retention. The alkyd type enamels previously described have proved very satisfactory.

### Bridges

The proper protection of a steel bridge receives much study from the railroad engineers. Protection of bridges is important for preserving the life of the structure and for accident prevention.

The paint most generally used is one or two coats of red lead primer and two coats of black graphite or carbon black paint.

The red lead used is approximately this formula:

28 lb. red lead (95%  $Pb_3O_4$ ).  
 1 gal. linseed oil.  
 $\frac{1}{8}$  gal. drier and volatile thinners.

The black graphite and carbon black paints are made to suit the different specifications of the railroads. Here are typical specifications:

#### BLACK GRAPHITE BRIDGE PAINT

Graphite .....	36.0%
Red lead .....	8.0%
Linseed oil .....	48.0%
Drier and volatile thinners .....	8.0%
	<hr/>
	100.0%

Graphite must be natural amorphous material that should contain not less than 35 per cent of graphite carbon.

#### CARBON BLACK PAINT

Pigment .....	30.0%
Vehicle .....	70.0%
	<hr/>
	100.0%

<i>Pigment</i>		<i>Vehicle:</i>	
Carbon black (or lampblack or a mixture .....	50.0%	Raw linseed oil .....	90.0%
Red lead .....	10.0%	Drier and thinner .....	10.0%
Extender pigments .....	40.0%		
	<hr/>		<hr/>
	100.0%		100.0%

Sometimes the vehicle is all raw linseed oil, in which case the railroad adds the drier on the job.

The two formulas given will produce very good paints if properly made. It is difficult to detect the purity of the graphite and of the carbon blacks; therefore the manufacturer may use some of the so-called mineral blacks or ground coals, which are inferior to a mixture of carbon black and silicates.

A formula which has given excellent service on bridge work is based on the following specification:

Pigment .....	30.0%
Vehicle .....	70.0%
	<hr/>
	100.0%

<i>Pigment</i>		<i>Vehicle:</i>	
Carbon or lampblack .....	20.0%	Linseed oil .....	90.0%
Red lead ( $Pb_3O_4$ ) .....	5.0%	Drier and volatile thinner .....	10.0%
Black iron oxide ( $Fe_3O_4$ ) .....	75.0%		
	100.0%		100.0%
Total of carbon, $Pb_3O_4$ , and $Fe_3O_4$ should be 97% minimum.			

This specification has the advantage of being almost tamperproof. In other words, it is a simple formulation that calls for pure raw materials. The paint is easy to make and to control, and any adulteration can be easily detected.

The value of this paint over the graphite formulation is obvious. Iron oxide, especially  $Fe_3O_4$ , is unquestionably much more rust-resistant than any carbon black or graphite pigment. A black paint made with the above pigment composition is good for any steel structure or steel equipment.

A good protective coating for steel would be one coat of anti-corrosive primer and two coats of black oxide paint.

For the second coat, some railroads prefer a maroon-colored paint instead of black. This is useful, because it will show plainly whether the third coat is omitted. This color is usually obtained by replacing some of the extender materials or some of the black oxide with a red or a brown iron oxide pigment.

If the bridge is to be painted white or a light color, the station paint formulations are very satisfactory, over a red lead or an iron oxide-zinc chromate primer. A chromate primer should be used if an aluminum finish is required. Aluminum paint for steel structures should be made with a vehicle such as Federal Specification TT-V-81 or TT-V-121a reduced to 45 or 50 per cent non-volatile, or with a pure phenolic varnish, or with a phenolic modified with some good alkyd liquid.

A straight air-dry type of alkyd liquid will lack the waterproofness that is best for this type of finish. The addition of a phenol formaldehyde-tung oil varnish will increase the water resistance and its drying qualities.

In the opinion of the author, the outstanding fault of railroad coatings lies in the policy of specifying the exact ingredients of a paint. Specifications, as a rule, become out-of-date and keep the paint manu-

facturer from supplying superior products which do not contain the specified materials. Since scientific development is the keynote of American industry, it would be better for railroads to buy from reputable manufacturers who can supply up-to-date products and technical advice from experts who are continually developing better products.

## CHAPTER 14

# THE FINISHING OF AUTOMOTIVE EQUIPMENT AND OTHER METAL SURFACES

FREDERICK G. WEED

### HISTORY

Before 1925, manufactured products using organic finishing materials were coated largely with oleoresinous or varnish type finishes. Many years of conscientious research and development work have resulted in the present high-speed methods of finishing, as used in the manufacture of automobiles, refrigerators, radio cabinets, and other widely used mass production articles.

With the advent and popular use of the automobile, the washing machine, the modern refrigerator, the radio, etc., the industry called for a new and more exacting type of finish. New finishes were necessary to create a greater appeal to the potential customer, and more enduring types were required to meet the special conditions of the refrigerator and washing machine.

It stands to reason that these improvements were not accomplished by a single stroke of luck but rather were the result of painstaking and carefully planned research.

Until the year 1925, automotive finishes were made by grinding the pigments then available in a varnish usually composed of linseed and wood oil cooked with a copal or other natural resin. About this time a new resin was introduced derived from a condensation of phenol and formaldehyde and modified with rosin. The trade knew these products as a modified Bakelite or Beckacite. Advantages of phenolic resins are, first, speed of surface and through drying; second, increased water resistance; third, greater outdoor durability as compared with natural resins; fourth, greater chemical resistance as compared with natural resins.

Low viscosity nitrocellulose was introduced in 1922, but the growth of the lacquer industry was due not only to the quantity production

of low viscosity nitrocellulose but also to the discovery of methods for quantity and low cost production of butyl alcohol by the Weizmann fermentation process of corn, which was perfected during the years 1923 and 1924. Thus the tremendous growth in usage of nitrocellulose finishes started in 1924 and 1925, with the additional inherent advantages of remarkably fast drying and improved durability and appearance of these finishes as compared with previously known types. Vast savings in floor space and finishing costs were possible with the use of lacquer finishes, which could be sprayed, one coat over another in intervals of 5 to 15 minutes, and then rubbed to a smooth, gloss finish several hours after application of the last coat.

A short time after the introduction of this material, substantial progress was made in the pigment field. This early work finally resulted in the development of our present high-grade maroon pigments as well as chromium hydrate, various organic yellows, phthalocyanine blues, and other durable types of pigments.

Considerable research work was also done on improving the white pigment known as titanium dioxide. Because of its great hiding power, this pigment was often used with colored pigments to obtain the shades desired. However, one of its great drawbacks was its tendency to chalk freely, thus affecting the tint retention and durability of the finish.

An examination of some old exposed panels demonstrates that considerable chalking took place with some of these old types of formulation. Work was now undertaken to introduce certain plasticizing and resin materials to enhance the durability and in other respects to minimize this chalking tendency. Glyptal (glycerol phthalate) was introduced on a substantial scale, after it was demonstrated through experimentation that the durability characteristics were improved to a marked degree.

In connection with the durability study, it may not be amiss to point out that the introduction of subtropical testing (Miami, Florida) played a very important part. The writer established a testing field at the University of Miami located at Coral Gables early in 1928.\* Since that time the importance of subtropical testing has been almost universally recognized. Further details of the weathering characteristics of materials are given under a separate heading.

\* This testing field has been conducted since its establishment under the personal direction of Dr. O. J. Sieplein (at present the director of the Miami Sun-Ray Research).



FINISHING METHODS OF ARTICLES MANUFACTURED  
BY INDUSTRIES

1. *Automotive.* The present method of finishing automobile equipment is divided into four parts:
  - a. Automotive equipment finished in lacquer.
    1. The refinishing of automotive equipment in nitro-cellulose lacquers.
  - b. Automotive equipment finished in synthetic (baking type).
  - c. Commercial vehicle finishing.
  - d. Air-drying synthetic enamels for refinishing.
2. *Refrigerator.*
3. *Washing machine.*

## AUTOMOTIVE FINISHING

**Automotive Equipment Finished in Lacquer**

The first step in the application of any paint on a large production scale is the preparation of the metal, i.e., the removing of grease, oil, and other foreign matter, and also the cleaning of the metal and removing of any rust which may be present on the surface. The many systems employed for this process usually contain a solvent (alcohol) and phosphoric acid. They are known to the trade by such names as Dioxidene, Rusticide, Metalprep, Bonderite, and Metal-Kleen.

The Bonderizing System is employed by several large automotive plants. This process may be described as follows:

1. **Scope.** The Spra-Bonderite Process is a chemical treatment for metal surfaces such as steel, galvanized iron or Galvannealed, zinc base die castings, cast iron, and cadmium. The treatment converts metallic surfaces to a non-metallic phosphate coating of the proper texture adapted to inhibiting corrosion and to increasing the adhesion and durability of any paint finish applied thereon. This increase in the durable life of the paint finish applied over the Bonderite coating is due to:

1. Insuring a chemically clean, grease-free surface for paint.
2. Providing a corrosion inhibiting surface on which to paint.
3. Providing a non-conducting bond between the base metal and the paint.

**2. The Process.** The Process Treatment consists in spraying the properly cleaned metal with a hot solution of Spra-Bonderite for a sufficient length of time (1 to  $1\frac{1}{2}$  minutes) to convert the metal surface to a uniform, protective Bonderite coating. The solution is forcefully sprayed on the work by means of equipment consisting of a pump and a series of spray pipes and nozzles so arranged that impingement is obtained on all surfaces. The solution is collected and recirculated continuously and is maintained at an operating temperature of 180° F. (82.2° C.). After Spra-Bonderizing, the work is properly rinsed and prepared for the final paint finish.

**3. Makeup.** For preparing the original process solution and for making up losses of solution due to leaks or cleaning out the tank, use Spra-Bonderite Makeup Chemical. The process solution is prepared by adding 50 pounds of Spra-Bonderite Makeup Chemical to each 100 gallons of water and heating to 180° F. (82.2° C.). The strength of the solution or the amount of total acid phosphates present is determined by titrating a 10-cc. sample with *N*/10 sodium hydroxide (testing solution) to neutrality, using phenolphthalein as an indicator. The presence of a permanent pink color indicates the end point of the titration.

A solution prepared as above will require approximately 10 cc. of *N*/10 sodium hydroxide (testing solution). It is known as a "10 point" solution.

**4. Replenishing.** For replenishing the solution due to the formation of the Bonderite coating on metal use Spra-Bonderite Replenishing Chemical. As metal is treated in the Spra-Bonderite solution, metallic acid phosphates, free phosphoric acid, and accelerator are used up in the formation of the Bonderite coating. The bath must be replenished from time to time with Spra-Bonderite Replenishing Chemical in order to maintain the solution at the proper operating strength. For each point drop in solution strength caused by the processing of work, 1.75 pounds of Spra-Bonderite Replenishing Chemical are required to restore each 100 gallons of solution to its original strength.

Frequent small additions of Spra-Bonderite Replenishing Chemical naturally produce a more uniform coating than occasional large additions. It is desirable to control and maintain the processing solution so that not more than one "point" variation in chemical strength will occur.

**5. Cleaning of the Metal.** All metal to be Bonderized should be free of grease and oil and should not contain any heavy rust or loose

scale. The cleaning may be done in a spray type washing machine using an ordinary alkali cleaning solution, or by a vapor degreaser.

When the cleaning is done with a spray type alkali washing machine, the concentration of the cleaning solution is important if an adherent, uniform, and finely crystalline Bonderite coating is to be obtained. Strong alkali cleaning solutions containing appreciable caustic tend to cause a rough Bonderite coating on metal commonly referred to as "sparkle." Such coatings are more absorptive than finely crystalline Bonderite coatings and, when painted, tend to dull the luster of the paint finish. So-called mild alkali cleaning compounds at concentrations of  $\frac{1}{4}$  to  $\frac{1}{2}$  ounce per gallon are recommended for use in the washing stage. It is essential that the cleaning solution be maintained at 180° F. (82.2° C.) or at such temperature that adequate cleaning will be obtained. In order to facilitate the cleaning of the metal, the surface may be wiped with a cloth damp with naphtha, mineral spirits, kerosene, or a similar solvent prior to the alkali cleaning operation. This wipe insures a uniform smooth Bonderite coating and reduces the consumption of chemicals.

After cleaning in the alkali washing stage, the work should be rinsed in one or preferably two spray stages of water maintained at 180° F. (82.2° C.) and overflowing to keep them clean and free of scum.

When the cleaning is done by vapor degreasing, the work before Bonderizing should be wiped or forcefully sprayed with hot water to remove any residue remaining on the surface.

**6. Cold Water Rinse.** After the Bonderizing operation, the work is rinsed in water for 30 to 60 seconds. The flow of water through the water rinse should be regulated in conjunction with the rate of production so that at no time will the main body of the rinse become contaminated.

**7. Chromic Acid Rinse.** Immediately after the water rinse, the work is rinsed for not less than 30 nor more than 60 seconds in a dilute solution of chromic acid at 180° F. (82.2° C.).

The chromic acid rinse is prepared by dissolving approximately 7.5 ounces of chromic acid in each 100 gallons of rinse solution. In localities where the water is hard, the amount of chromic acid will be somewhat greater than required with soft water. When first prepared, a 25-cc. sample should give a titration of 1.0 cc., using *N*/10 sodium hydroxide and about 2 drops of methyl orange indicator. The end point of the titration is a change from the original reddish-orange color to yellow. By adding five drops of phenolphthalein indicator and continuing the titration until a pink color of 15 seconds' duration is pro-

duced, a total reading of 2 to 2.5 cc. is obtained. Owing to continued use, the rinse will become contaminated with Bonderizing salts. This will be evidenced by an increase in the second titration. During its use, the rinse should be maintained at a strength of 1.0 cc. according to the first titration, by additions of chromic acid. Whenever the rinse is maintained at 1.0 cc. according to the first titration, the second titration should not exceed 7.5 cc.

**8. Drying.** The Bonderized articles shall be dried immediately after the rinse operation by means of a dry-off oven.

**9. Characteristics of the Process.** For continuous and satisfactory operation of the Spra-Bonderite Process, it is essential to have at all times an adequate volume of processing solution sprayed onto the work during the processing interval. This condition can be obtained only by keeping the spray nozzles clean and not permitting them to become clogged. Once suitable spraying conditions have been established when the equipment is placed in operation, it is necessary that these conditions be maintained by establishing periodic inspection and cleaning schedules to insure that the nozzles do not become clogged, thus reducing the spraying efficiency.

As scale forms on the heating coils, it will be necessary to remove them from time to time and hammer off the scale in order to maintain the proper solution temperature.

In the operation of the process, sludge is formed as a by-product in the Bonderizing operation and collects in the bottom of the tank. This sludge should be removed whenever its presence interferes with the operation of the spraying system. A convenient method for removing the sludge consists in allowing it to settle and pumping the Bonderite solution into a separate tank, whereby the sludge can be easily removed from the bottom of the processing tank. Any Bonderite processing solution losses during the cleaning operation should be restored by the addition of Spray-Bonderite Makeup Chemical.

After the tank is cleaned, the solution is returned to the tank and the tank is refilled to operating level with water heated to 180° F. (82.2° C.) and then thoroughly mixed, after which the solution should be tested. For each "point" in strength below that strength determined just before starting the clean-out, 5 pounds Spra-Bonderite Makeup Chemical should be added for each 100 gallons of solution.

### **10. Summary.**

1. Use 50 pounds of Spra-Bonderite Makeup Chemical for each 100 gallons of water to build up the original solution.

2. To test the Bonderite solution, pipette 10 cc. of the solution into a beaker, add 3 to 5 drops of indicator (phenolphthalein), and run in testing solution ( $N/10$  NaOH) until a pink color develops. The number of cubic centimeters of testing solution required is the strength (points) of the Bonderite solution.

3. Operate the Spra-Bonderite solution at 10 "points."

4. Use 1.75 pounds Spra-Bonderite Replenishing Chemical for each 100 gallons of processing solution per "point" to restore chemical strength lost through processing work.

5. Maintain the solution temperature at around 180° F. (82.2° C.) while processing.

6. Time of processing is 1 to 1½ minutes.

7. Remove sludge from processing tank whenever its presence interferes with the successful spraying of the solution.

8. Remove scale from coils before difficulty is encountered in maintaining desired operating temperature.

9. Restore losses in solution strength due to *mechanical causes* by adding 5 pounds Spra-Bonderite Makeup Chemical per 100 gallons per "point" loss of strength.

10. Maintain the circulating system and sprays in good working condition at all times. Keep spray orifices open.

11. Trouble in Bonderizing is most frequently caused by improper cleaning, operation of the solution below recommended temperature, or insufficient replenishing to maintain the solution at the proper operating strength.

The thorough cleaning of the metal by the Bonderite process effectively removes all soldering flux, acids, etc. The above process of metal cleaning may be described as **Operation One** in the production line.

**Operation Two: Spray Primer (Oil Type).** The entire body, inside and out, is sprayed with a metal primer. Great care is exercised to see that the backs of doors, hinges, body sills, and metal flanges on windows and on window sills are all carefully covered. The outside of the body is sprayed with a uniform coat, care being taken to apply the material not too heavily. It has been found that heavy coats impair rather than assist the bonding or adhesion, one of the more important requirements of a primer.

The body now passes through a conveyor oven, the effective baking time being one hour at 200° F. (93.3° C.). (*Note:* The actual baking curve on an average prime oven will probably show a peak of 225° F.

(107.2° C.) tapering off to 175° F. (79.4° C.). The average of one hour at 200° F. (93.3° C.) is adequate for the baking of the usual metal primer.)

**Operation Three: Application of Surfacer or Glaze Coat (Oil Type).**

Where deep file marks show as a result of metal finishing, a heavy spray coat of surfacer is applied. This is followed immediately with a double coat of surfacer overall. The body now enters the conveyor oven for a minimum effective bake of one hour at 210° F. (98.9° C.); actual peak heat in the oven may run as high as 245° F. (118.3° C.) for a short space of time.

**Operation Four: Water Sanding.** After the body has been thoroughly dried and cooled, the entire outside surface is water-sanded. The fineness of the sandpaper varies but generally No. 320 paper is used. Great care is exercised to prevent cutting through to the bare metal, and special attention is given to all the detail work around moldings and window inserts.

After complete sanding, the surface is washed and inspected. Any surface spots which have been missed are now detailed by an operator specially designated for that purpose. The body now goes through a dry-off oven.

**Operation Five: Drying and Tacking.** Water is blown out from around the hinges, door and body facings, and tops of doors with a compressed air fitting. The presence of any moisture at this point has a very deleterious effect on the adhesion of subsequent lacquer coatings. Any bare metal spots which show as a result of sanding through are touched up with pyroxylin primer and allowed to air-dry several minutes. The presence of any deep impression, such as a solder pit around the soldered areas, is taken care of by knife glazing with pyroxylin putty followed by a scuffing operation. The entire surface is now tack-ragged to remove all dust and other accumulations. (*Note:* The application of both primer and surfacer varies with the individual plant. Generally speaking, however, the material is applied as received in the package, approximately 90 pounds of air being employed to atomize the material and 10 to 15 pounds to bring the material up to the nozzle.)

**Operation Six: Application of Lacquer.** The lacquer is applied by spraying. The viscosity of the material varies from 15 to 20 seconds as measured on the No. 4 Ford Viscosity Cup. The thinner reduction, naturally, varies with the color employed, but, generally speaking, the amount of reducer added to the lacquer varies from one part thinner to one part lacquer to two parts thinner to one part lacquer. The

main objective is a smoothly applied coat free from what is commonly called orange peel or other roughness on the surface. This lacquer coat is force-dried from 7 to 10 minutes at 170° F. (76.7° C.).

**Operation Seven: "Dinging."** Low spots in the metal may now be easily seen as a result of the glossy lacquer coat, and "dingmen" with tools specially designed for the purpose remove these imperfections by "dinging" and bumping. Other imperfections in the surface, such as occluded dirt, are carefully sanded out at this point.

**Operation Eight: Additional Lacquer Coats.** Three additional lacquer coats are applied by spraying, several minutes between coats, and the body now passes into the final force-drying operation of approximately 30 minutes at 180° F. (82.2° C.).

**Operation Nine: Installation of Upholstery.** The body now passes into the trim shop where the upholstery is installed.

**Operation Ten: Polishing of Body.** The entire upper portion of the body, which includes the window reveals, hinges, and other detail, is completely oil-sanded with 320 paper. The bottom portions are buffed with a mechanical buffer. This mechanical buffer consists of a round felt disk, approximately 8 inches in diameter. A cutting or polishing compound is employed to aid in the polishing of the surface.

**Operation Eleven: Touch-up and Final Inspection.** The body is now striped with a mechanical striper in a contrasting color, after which the entire surface is inspected for defects and slicked up and polished preparatory to shipping.

### The Refinishing of Automotive Equipment in Nitrocellulose Lacquers

General reference has been made to the improved production and the greatly reduced time element resulting from the introduction of nitrocellulose lacquers into the original finishing of automotive equipment. A corresponding improvement in the refinishing of automotive equipment has resulted in the use of nitrocellulose lacquers. The refinishing phase has assumed rather impressive proportions in late years because of universal automotive transportation, the large trade in used cars, involving their renewal, and the complete list of refinishing materials available for *quick* and complete overall finishing or spot touch-up.

Obviously, the limitations of this review prevent presentation of the entire scope and varying phases of general refinishing operations. For instance, the introduction of aluminum, in recent years, to attain iridescent color effects, the control of these effects in the spraying operation, the improved nature of maroon pigments with reference to

color stability and consequent ease of renewing and refinishing cars in what were formerly difficult and uncertain maroon tones, the use of combination primer-surfacers, and the introduction of the high synthetic resin content lacquers are but a few of the features that have contributed to the creating of this large and continually expanding field of automotive refinishing.

Three standard rather arbitrary refinishing procedures are outlined here. The first is a complete refinishing where the former finish has been removed. The second is a complete refinish over the old without removal of the former finish. The third is a touch-up or partial refinish over the old surface.

### **Complete Refinishing of Automobile. System 1.**

1. Completely remove former finish. Use either solvent removers, such as those made from benzol, acetone, and alcohol mixtures; alkali and hot-water removers; or the blow-torch process (often referred to as "burn off"). The solvent removal method is in most common use for metal bodies.

2. Wash completely with a phosphoric acid solution such as Metal-prep, Deoxidine, or equal. Proper diluting directions appear on the container. This etches the metal, prevents rusting, and gives a better bond for the succeeding primer coats. Care should be taken not to touch the job with bare hands or soiled cloths after this acid wash.

3. Apply lacquer primer—a thin, uniform coat gives best results. Allow 30 minutes for proper drying.

4. Apply two double head coats lacquer surfacer reduced to proper consistency. Allow first coat to flash out before applying second coat. Allow 30 minutes for complete drying.

5. Water sand with No. 240 paper and finish with No. 320. Low spots or imperfections should be puttied and glazed.

6. Apply one double-head coat properly reduced finishing lacquer. Allow to dry 10 to 15 minutes. Apply second double head coat of finishing lacquer. Allow to dry 2 to 3 hours.

7. Rub surface with standard rubbing compound and polish to proper luster.

### **Complete Refinishing of Automobile. System 2.**

- 1 and 2. Same as Operations 1 and 2, System 1.

3. Spray two double head coats of a lacquer primer-surfacer reduced as per directions. Allow to dry 30 minutes.



4. Sand with No. 240 or No. 280 sandpaper, wet or dry, and finish with No. 320. Low spots or imperfections should be puttied and glazed.

5. Complete as in Operations 6 and 7, System 1.

### **Refinishing Where Original Finish Is in Fairly Good Condition. System 3.**

1. Sand old finish with No. 320 sandpaper. Wash entire surface with precleaner and wax remover, and inspect for bare spots.

2. Spray two coats of lacquer primer-surfacer reduced as per directions on all repaired spots and cut-throughs. After drying sufficiently, sand repaired portions smooth with No. 320 sandpaper.

3. Apply two double head coats finishing lacquer reduced as per directions. Allow to dry 2 to 3 hours.

4. Rub surface with standard rubbing compound and polish to proper luster.

### **Automotive Equipment Finished in Synthetic Baking Enamel**

In considering the newest method of finishing bodies, one cannot help but think of the methods of twenty years ago which were laborious and time-consuming. Although the time of finishing a body has been reduced substantially, one must not forget that this has not been done at the expense of the ultimate user, who, at the present time, is receiving more satisfaction for his dollar invested because of the superior qualities of the finish.

The finishing schedule used on bodies in a modern motor plant is a surprisingly small fraction of the time required when the early motor cars were given their decorative coatings with varnish materials and, consequently, is responsible for great savings in cost to the consumer. A modern schedule requires around twelve hours from the time a body is delivered to the paint shop until it is ready, fully trimmed and painted, to be set in place on the chassis, which is moving along the assembly line, soon to be part of the completely built motor car. Contrast this with 552 hours required in the same plant less than twenty years ago.

Along with the rapid decrease in the elapsed hours has come an almost proportionate increase in the quality of the decorative and protective finish with resulting benefits to the consumer. Not only can he obtain an almost unlimited selection of colors but also he will have a finish which will withstand drastic exposure in all seasons of the year and in almost any climate. He will find that the finish will

retain its color and luster to a most remarkable degree and that it can be kept clean with a surprisingly small amount of effort. Furthermore, he will find that the steel itself has been chemically treated to prevent the spreading of destructive rust formation from any localized part of the finish should it become damaged.

When considering the underlying reasons which have contributed to the development of such a comparatively short finishing schedule, reference to the schedules shown later on will almost immediately disclose that the greatest individual item has been the substitution of forced mechanical drying methods for the ordinary natural air drying at room temperatures previously employed. The knowledge that chemical reactions are greatly accelerated at higher temperatures was first adopted to this problem. Then applied research developed organic resins which not only dried to hard flexible films through the process of oxidation but also were heat-hardened through the chemical process of polymerization. The use of these synthetic resins has permitted the force drying of all undercoatings and finish coatings in a minimum of time. It is necessary to place limits on bake oven temperatures because of the method of fabricating steel bodies. For example, a large quantity of solder is employed in filling around the welded joints. Moreover, the stability of many pigments used in conjunction with the resins to make the colored finish coats is affected by overheating. The most delicate color shade, by virtue of its susceptibility to this color change at an elevated temperature, will determine the maximum temperature which can be used with safety.

Improvement in mechanical equipment, engineering design, and adoption of the progressive assembly method of manufacture have also played most important parts in the development of modern efficient painting methods.

1. Conveyor systems now efficiently handle all units from one operation to the next.

2. A body is now completely trimmed in 2 hours whereas 72 hours were formerly required.

3. The cleaning and chemical treatment of the steel body are done in mechanical washing machines.

4. The paint is pumped from a central mixing room through pipes to those points where it is to be used.

5. All paint materials are applied with spray guns.

6. Elaborate air washing and cleaning systems keep out dirt from spray booths and drying ovens, thereby improving the working con-

## 442 FINISHING AUTOMOTIVE AND OTHER METAL SURFACES

ditions for the employees and at the same time making the finished paint job smooth and clear.

Each of the above points represents a vital part of the aggregate.

Naturally, careful planning, proper scheduling, and trained supervision have also contributed to making a short efficient schedule a daily operating possibility.

Following is presented a varnishing finishing schedule for bodies used in 1920:

OPERATION	TIME REQUIRED
1. Clean—Sand off rust with emery cloth.	
Wash body completely with naphtha.	
Spray primer coat.	
Dry overnight.	24 hours
2. Knife-putty-glaze entire body.	
Dry until morning of second day.	48 hours
3. Spray first coat of rough stuff.	
Dry overnight.	24 hours
4. Spray second coat of rough stuff.	
Dry overnight.	24 hours
5. Spray third coat of rough stuff.	
Dry overnight.	24 hours
6. Rub to surface with brick and pumice stones.	
Spot putty defects in surface.	
Dry overnight.	24 hours
7. Spot sand putty.	
Brush sealer coat on entire job.	
Dry overnight.	24 hours
8. Brush color ground.	
Dry overnight.	24 hours
9. Brush first coat of color varnish.	
Dry until morning of second day.	48 hours
10. Brush second coat of color varnish.	
Dry until morning of second day.	48 hours
11. Rub varnish to surface using pumice stone, felt, and water.	
Color putty small defects in surface.	
Dry overnight.	24 hours
12. Brush third coat of color varnish.	
Dry until morning of second day.	48 hours
13. Trim body.	48 hours
14. Rub varnish with pumice, felt, and water.	
Stripe body.	
Dry overnight.	24 hours
15. Assemble interior hardware such as window moldings.	24 hours
16. Water rub slickup with pumice and felt.	
Wash with naphtha; clean surface with mixture of olive oil, gasoline, and water.	

## OPERATION

Touch up edges; color-putty very small spots.	
Dry overnight.	24 hours
17. Tack rag surface.	
Seal all crevices with shellac.	
Tack rag.	
Brush finishing varnish.	
Dry in dark room until morning of second day.	48 hours
Total elapsed time	552 hours
Equivalent to	23 days

Compare the above schedule with the enameling schedule for Bodies used in 1939 which is:

OPERATION	TIME REQUIRED
1. Spot-clean body and wipe door facings.	
Automatically wash with alkaline solution.	
Automatically rinse with hot water.	
Automatically rinse with hot water.	
Automatically spray hot Bonderite solution.	
Automatically rinse with hot water.	
Automatically rinse with chromic acid solution.	
Dry off oven 15 minutes, 300° F. (148.9° C.).	
Cool.	1.00 hour
2. Spray two coats combination primer and surfacer. Use one coat immediately after the other.	
Bake 60 minutes; peak temperature 275° F. (135° C.).	1.25 hours
3. Sand to surface with waterproof sandpaper and water.	
Dry off oven 15 minutes, 250° F. (121.1° C.).	
Inspect for repairs and dings.	
Repair dings.	
Spot-knife-putty any glaze defects in surface.	
Dry off oven 10 minutes, 150° F. (65.6° C.).	
Seal inside of body and apply silencer materials.	
Spot sand putty.	2.50 hours
4. Wipe body with naphtha.	
Tack rag.	
Spray enamel sealer coat.	
Bake 60 minutes; peak temperature 275° F. (135° C.).	1.25 hours
5. Spray underbody.	
Repair metal for dings.	
Sand to surface with sandpaper and water.	
Dry off oven 15 minutes, 250° F. (121.1° C.).	
Spot sand defects.	
Slush inside of body.	1.50 hours
6. Wipe body with naphtha.	
Tack rag.	
Spray two coats of colored synthetic enamel.	

## 444 FINISHING AUTOMOTIVE AND OTHER METAL SURFACES

### OPERATION

Bake 45 minutes; peak temperature 260° F. (126.7° C.).	
Cool.	1.50 hours
7. Trim body.	2.00 hours
8. Spot sand scratches.	
Spray sanded areas with colored enamel.	
Bake 30 minutes, 180° F. (82.2° C.).	
Cool.	
Stripe body	1.00 hour
	<hr/>
Total elapsed time	12.00 hours

The enameling schedule for sheet metal parts, which include hoods, fenders, radiator shields, lamps, and brackets, is as follows:

OPERATION	TIME REQUIRED
1. Automatically wash with alkaline solution.	
Automatically rinse with hot water.	
Automatically rinse with hot water.	
Automatically spray with hot Bonderite solution.	
Automatically rinse with hot water.	
Automatically rinse with chromic acid solution.	
Dry off oven 15 minutes, 300° F. (148.9° C.)	
Cool.	0.50 hour
2. Automatically flow enamel sealer coat.	
Bake 45 minutes; peak temperature 350° F. (176.7° C.).	
Cool.	
Scuff sealer coat with sandpaper.	1.25 hours
3. Tack rag.	
Spray two coats of colored enamel, one immediately after the other.	
Bake 45 minutes; peak temperature 250° F. (121.1° C.).	
Cool.	1.25 hours
	<hr/>
Total elapsed time	3.00 hours

### Commercial Vehicle Finishing—Large Trucks and Vans

The finishing systems for automotive trucks of the small panel type and for passenger automobiles as already outlined are identical.

The finishing of large-sized trucks and busses, however, presents a somewhat varied system because the number built does not warrant a high-speed production set-up. Also, while no one system is universally used, the following system is generally acceptable:

1. Clean all metal and wood parts thoroughly.
2. Apply one brush coat of a long-oil lead primer to all wood parts.

3. Spray one double-head coat of synthetic base primer-surfacer on all metal parts.
4. Bake or air-dry overnight, depending on whether oven facilities are available.
5. Water-sand with No. 280 sandpaper and dry-scuff the wood parts.
6. Touch up any damaged spots with pyroxylin primer-surfacer.
7. Apply two or more coats of lacquer or synthetic enamel in the desired color, allowing sufficient time between coats to prevent sags.
8. Letter or stripe with synthetic enamel.
9. Apply decalcomania transfers. In preparing decalcomania transfers, only the lettering should be cut in with rubbing varnish. It is not advisable to brush the entire paper transfers. When the transfer has been applied, smooth out carefully and soak with water to remove the outside paper. The use of gasoline or turpentine should be avoided, especially if the finish coat is synthetic enamel. When the transfer is smooth and thoroughly dry, brush or spray with clear synthetic enamel to protect the surface of the transfer.

### **Air-drying Synthetic Enamels for Refinishing**

Synthetic automotive enamels may be divided into two distinct classifications: the air-drying types employed in the main by refinishing shops and for truck enamels and the baking types of synthetic enamels with which several large automotive manufacturers are finishing their entire production of automobiles and which have already been described. The baking types of synthetics are also used extensively as wheel enamels and on instrument board panels, steering columns, fenders, and on many other small parts of the car by manufacturers who employ pyroxylin type finishes on the body of the automobile proper.

The air-drying synthetic enamels require a type of fixed vehicle or synthetic resin which, when properly pigmented, the correct amount of drier added, and reduced with solvents and diluents to brushing or spraying consistency will set up sufficiently fast so as not to collect too much dirt on the surface of the enamel film. This setting up of the film is known as the tack-free time and/or the dust-free time, a condition which may occur within a few minutes or possibly take up the greater part of an hour. The film of such an enamel will, under ordinary procedure, dry in six to eight hours, or at least on standing overnight be sufficiently hard to permit tacking off the job for lettering or striping.

As previously stated, the air-drying enamels are employed to a large extent in the refinishing of automobiles, especially by garages that specialize in repairing and the bumping of damaged parts as well as refinishing the complete car. The enamels are used chiefly because of their ease of application and the fact that after drying they produce a finish with a high gloss or luster and require no polishing or rubbing by the finisher.

The following system of preparing and the handling of cars prior to the painting or spraying operation, as well as the actual refinishing of the car as recommended by one of the large manufacturers of this type of enamel, is given as a guide to those who may be interested in this type of finishing.

**1. Washing.** The entire car should be carefully washed, being absolutely sure to remove all of the muddy accumulation from chassis and under fender portions. To facilitate cleaning, wheels may be removed. The heavy deposit of grease and dirt under the chassis portion can be removed with a stiff brush, with gasoline as the solvent. (Strong washing powders and hot water have also been found very effective in removing grease. Trisodium phosphate in the proportion of 4 ounces of material to 1 gallon of water has also proved very successful.) It is very essential that all the grease and oily substances be removed before finishing any parts; otherwise drying and adhesion will be retarded.

**2. Dismantling.** All removable parts are taken off. In addition to the wheels, they include spare tires or extra wheels, hood, and any loose hardware such as door handles and horns.

**3. Dinging out Dents.** Fenders and body dents should be dinged and sanded with a sanding disk to smooth out and remove any rust accumulations.

**4. Preparation of the Old Surface.** The entire surface is water-sanded with No. 280 paper. Very careful sanding of all reveals and seams of the moldings and other indentations is recommended to remove the waxy accumulations and road dirt. The sanding operation also roughens the surface, which will promote the adhesion of the enamel to the surface as well as aid in removing the wax.

**5. Touch-up.** On completing the sanding, the bare metal portions and other imperfections in the surface should be thoroughly cleansed with a precleaner and wax remover type of solvent. This is usually composed of a mixture of coal tar hydrocarbons (xylol and toluol) and carbon tetrachloride and turpentine. The spots should then be sprayed

with an air-drying synthetic primer-surfacer or a pyroxylin type primer-surfacer. If speed is required, the pyroxylin primer-surfacer will be more satisfactory as it may be sanded in a short time after application, whereas the synthetic undercoat requires four hours to dry before sanding.

**6. Masking In.** Windows, rubber running boards, and any hardware that has not been removed are covered with paper and masking tape. The radiator grille and lamps should also be covered, unless they are to be finished along with the car.

**7. Sanding of Repaired Portions.** The repaired portions are dry-sanded with No. 280 paper, care being taken to feather out completely. Water sanding is recommended as an alternative system where time is not so important a factor, in which case No. 320 paper may be used.

**8. Cleaning Wheels.** The wheels should be carefully cleaned, using a strong soap solution or a stiff-bristled brush and gasoline in order to remove accumulations of dirt and grease. After the completion of this operation, the wheels are allowed to become thoroughly dry and are ready for finishing.

**9. Sealing.** Sealing in of all cracks, crevices, etc., is recommended and this should be done using the same color as is to be used on the job itself. The accompanying list covers the majority of places where special care should be taken to produce an excellent finished job.

*a.* Sealing is started at the radiator and all cracks and crevices of the adjoining fender.

*b.* Front of cowl and ventilator if present.

*c.* Right door jambs and roof. In connection with the application of material to the door jambs on the right, it is recommended that the opposite door be thrown open to allow the passage of fumes through the car.

*d.* Loose drip moldings and top deck. Spray light coat on top deck.

*e.* Trunk covers are raised and sealed completely underneath and all fender welts carefully sealed.

*f.* Running boards, together with the paper covering. (A light sealing coat of material effectively ties in all loose dirt falling thereafter on the paper.)

*g.* Crack between body and splash aprons near the running board. This is very essential.

*h.* Left door jambs. Same operation to be repeated as for the right door jambs.



i. Chassis is thoroughly covered with the color employed on the body (if black is indicated for this operation, it may be used at this point).

j. The hood is next sealed along the hinges and on the rear portion, special care being given to the louvers.

**10. Use of Precleaner and Wax Remover.** The use of a precleaner and wax remover cannot be too highly recommended at this point to remove the wax deposits, grease, and overspray from the sealing in operation. All surfaces should be treated. The precleaner may be applied literally one panel at a time and immediately wiped up dry with a clean cloth. Cleanliness should be the dominant factor at this point, and, needless to say, only clean cloths should be used and plenty of them. Care must be exercised to avoid the use of large quantities of precleaner over freshly surfaced spots. This will avoid lifting difficulties.

**11. Tacking Off.** Tack rags may be purchased on the open market ready for use, and may be stored in tightly covered cans for future use. All surfaces are carefully tacked off and made ready for the application of the enamel.

**12. Enamel Application.** The enamel is reduced to the spraying viscosity recommended by the supplier, and as each refinisher has his own style of spraying and his own spray equipment nothing further need be mentioned regarding this phase of the procedure. After the car has been sprayed, it is allowed to stand at least overnight, at which time the job may be assembled and striped, using a striping medium containing the same type of vehicle as the enamel used for finishing.

## THE FINISHING OF OTHER INDUSTRIAL EQUIPMENT

### Refrigerator Finishing

Refrigerator finishing like that of automobile, washing machine, and other present-day necessities presents a problem all its own. But, like the others, constant improvement in paint materials and systems has led to the present-day finish, which gives maximum economy, beauty, and durability.

Originally, the outside of the boxes was finished in vitreous enamel, but not only was the original cost high but also the danger of chipping and the resultant inability to repair were big factors against its continued use.

The industry then adopted a paint system of oil-base primer and phenol-modified alkyd resin base enamel. Both materials were baked, and they gave a system that appeared to be entirely satisfactory. It was found, however, that on aging the white enamel would not hold its color and gradually turned to a cream, owing to the phenol-formaldehyde modification.

To correct this difficulty, the refrigerator manufacturers changed to the use of an oil-base baked primer and an air-drying white lacquer. This system provided better color retention and also made spot repair work easy because of the ability of the lacquer to "soften back."

As progress was made in the further development and improvement of alkyd synthetic resins, the trend was gradually back to the baked synthetic enamel. This time, however, the resin was of the unmodified type—free of phenol or resin-modifying agents—and generally containing soybean as the fatty acid. This gave a very good, durable enamel and one in which the color retention was satisfactory.

With the advent of the urea-formaldehyde resins, characterized by their water-white color, extreme hardness and resistance to acids, alkali, and solvents, it was only natural that white enamels with urea resin as their base should fit in nicely with the refrigerator-finishing systems.

The generally accepted present-day system of refrigerator finishing, therefore, consists of phosphoric-acid-treated metal (either Grenadized, Bonderized, or Metalpreped) on which is sprayed a one-mil thickness of primer followed by a one-coat, one-mil thickness of gloss white enamel.

The prime coat is 100 per cent alkyd resin base and is given a bake of one hour at 360° F. (182.2° C.) or equivalent.

The gloss white enamel is of the urea-base, alkyd-modified type and is given a bake of 1½ hours at 280° F. (137.8° C.) or equivalent.

In checking the merits of a refrigerator-finishing system, the system is submitted to ten tests which are designed to cover every ordinary treatment which might be encountered in actual use. All the tests have been assigned an importance and a reject rating by means of which the various systems may be compared. The importance rating is determined by the probability of the finish being submitted to certain usage which is covered by each particular test. This rating gives the percentage importance of each test on a basis of 100 per cent for all tests.

The tests and their ratings are generally the following:

**I. Mechanical Characteristics.** Importance 20 per cent—Reject 80 per cent. Under this heading the film is checked for adhesion, flexibility, toughness, and resistance to chipping.

**II. Alcohol.** Importance 2 per cent—Reject 25 per cent. The reason for this test is obvious inasmuch as in many homes there is a possibility of alcoholic beverages coming in contact with the finish.

**III. Fruit Juices.** Importance 2 per cent—Reject 50 per cent. Because of the fact that fruits are often stored in the refrigerator, it is quite likely that their juices will come in contact with the finish.

**IV. Oleic Acid and Lard Oil.** Importance 10 per cent—Reject 75 per cent. There are a great many oils and greases which are likely to come in contact with the finish, but a mixture of the two named above provide as hard a test as any.

**V. Butter.** Importance 15 per cent—Reject 75 per cent. This is used as a supplement to the preceding test, as unsalted butter especially becomes rancid very easily and has a destructive effect on some finishes.

**VI. Sulfur Dioxide.** Importance 7 per cent—Reject 85 per cent. Finishing systems for refrigerators using sulfur dioxide as a refrigerant must have a high  $\text{SO}_2$  rating because of the possibility of a unit starting to leak and causing discoloration of the boxes.

**VII. Humidity Test.** Importance 20 per cent—Reject 80 per cent. Humidity resistance is very important especially on finishes which will be in service in the southern coastal regions. This test also serves as a check on water resistance and porosity of the finish.

**VIII. Heat.** Importance 2 per cent—Reject 60 per cent. The effect of heat cannot be overlooked because of the possibility of hot dishes or electrical appliances being placed on the top of the refrigerator.

**IX. Ultraviolet Ray.** Importance 12 per cent—Reject 80 per cent. This is an accelerated light test to give an indication of the color retention of the finish.

**X. Weather Test.** Importance 10 per cent—Reject 60 per cent. This test indicates the durability of the finish when a refrigerator is set out on a porch or perhaps beside an open window. The two main defects which show up on this test are color change and loss of gloss.

Below is given the system employed by a large manufacturer of refrigerators.

#### **Reduction for Application.**

*Prime.* Reduce with petroleum solvent to a viscosity of 16 seconds at 80° F. (26.7° C.).

*Enamel.* Reduce with petroleum solvent to a viscosity of  $20\frac{1}{2}$  seconds at  $80^{\circ}\text{F.}$  ( $26.7^{\circ}\text{C.}$ ).

*Note.* Viscosity tests made by using Ford viscosity cup with No. 4 orifice. For each  $10^{\circ}\text{F.}$  ( $5.55^{\circ}\text{C.}$ ) increase in temperature the viscosity readings should be 1 second lower, and for each  $10^{\circ}\text{F.}$  ( $5.55^{\circ}\text{C.}$ ) lower temperature the viscosity reading should be 1 second higher.

*Example:* at  $80^{\circ}\text{F.}$  ( $26.7^{\circ}\text{C.}$ ) viscosity  $20\frac{1}{2}$ .

$90^{\circ}\text{F.}$  ( $32.2^{\circ}\text{C.}$ ) viscosity  $19\frac{1}{2}$ .

$70^{\circ}\text{F.}$  ( $21.1^{\circ}\text{C.}$ ) viscosity  $21\frac{1}{2}$ .

Prime will show very little change in viscosity within plus or minus  $10^{\circ}\text{F.}$  ( $5.55^{\circ}\text{C.}$ ).

1. All metal parts to be run through degreasing and Bonderite tanks. Any rust that shows signs of etching the metal must be sanded off prior to degreasing.

2. Transfer metal from Bonderite to paint conveyor. Scuff exterior surface lightly with steel wool or fine emery cloth and tack-wipe ahead of prime spray booth. (All operators handling metal after Bonderiting and during entire painting operation must wear canvas gloves.)

3. Spray one medium coat filler directly over Bonderite metal finished surfaces of cabinet, such as ball corners of shell, door corners and edges of door, and strip at base of side panels where reinforcement strip welded on inside making necessary disk grinder operation on exterior surface.

4. Spray all exterior surfaces and include only the interior surfaces of the machine compartment and machine compartment door with one full cross coat (one pass) prime-reduced as specified. Film should not exceed thickness of 0.0012 or be less than 0.001.

5. Bake prime coat 60 minutes at  $360^{\circ}\text{F.}$  ( $182.2^{\circ}\text{C.}$ ).

6. Inspect metal for dents and ding where necessary.

7. Sand prime lightly with No. 240 dry sandpaper where necessary to remove dirt nibs. Any scratches in prime must be feather-edged until smooth. Any bare metal spots over  $\frac{1}{4}$  inch in diameter must be returned through prime operation and entire panel be re-sprayed and baked.

8. Tack wipe and spray one full cross coat (one pass) enamel reduced as specified. Film thickness should not exceed 0.0014 or be less than 0.001. Total film thickness should not exceed 0.0026 or be less than 0.002.

9. Bake finish coat 1 hour and 40 minutes (effective bake) at 280° F. (137.8° C.). (Average of twelve oven-controlling instruments.)

10. Inspect for paint defects after finish coat bake.

11. Feather-edge rejected panels where necessary and return to paint conveyor ahead of prime spray booth.

12. Spray bare metal spots with prime (reduced as previously specified).

13. Follow on through entire painting procedure as previously outlined.

*Note.* In priming bare metal spots on panels to be reworked, it will be necessary to prime only over the bare metal spots on finished and intermediate coat work, but on primed metal the entire panel must be resprayed.

The extra bake on the finish coat will not be harmful as the enamel must be hardened before refinishing, but the prime is already baked at such a high temperature that the second bake would be too much.

### **Washing-Machine Finishing**

The washing machine, formerly hidden away in a dark basement to be resurrected on Monday morning for the family washing, now has rightfully been placed among the other household utilities—the refrigerator, the stove, the metal kitchen cabinets, in a sanitary, well-lighted utility room adjoining the kitchen—there to do its part in the job of keeping the home clean, sanitary, and beautiful. This transformation is due, in part, to the consideration given to superstyling and attractive appearance by the washer manufacturers today.

The white, porcelainlike finish on the modern washing machine is strictly chemical in nature. It may be a glycerol-phthlate resin or a urea-formaldehyde resin or a combination of the two. In most cases, the finishes are baked at a medium to high temperature in well-ventilated, air-conditioned ovens.

The machines, after being assembled and tested, are given a phosphate wash, a rinse, are dried, and sent to the finishing room for a first coat or primer. The priming coat is designed primarily to protect the metal against rusting and to provide a satisfactory surface on the metal for subsequent coats of enamel. The primer must withstand several thousand hours in the humidity cabinet, be unaffected by mild alkali, and must offer good “hold out” to the finish coat which will follow. The undercoat is usually baked at a high temperature

(350 to 400° F. or 176.7 to 204.4° C.), which helps to make it resistant to early failure. The machines are sanded, wiped free of lint and dust, and are then ready for the final coat.

The enamel or finish coat is sprayed as soon as the machines are cooled after coming from the primer oven. The washers enter at one end of the spray room, passing slowly through the spray booths where a full coat of synthetic enamel is applied. About five minutes after being sprayed, the machines enter the oven where they are baked for 30 to 60 minutes at 250 to 280° F. (121.1 to 137.8° C.).

A typical specification for testing a washing machine finish is similar to the following:

<i>Dry.</i>	Must be hard when baked at the standard time and temperature.
<i>Gloss.</i>	Shall be equal to a standard set up between supplier and user of the material.
<i>Cleanliness.</i>	Shall be absolutely free of dirt, lint, and grit.
<i>Humidity.</i>	Panels prepared in the standard system must stand 1,000 hours in a humidity cabinet in which the temperature ranges from 106 to 110° F. (41.1 to 43.3° C.) and the relative humidity is 100 per cent without showing loss of gloss or loss of adhesion.
<i>Hardness.</i>	Shall be determined by use of a Sward Hardness Tester. Should run 30 to 40 per cent when gloss equals 100 per cent.
<i>Soap or Alkali.</i>	Three to four inches of a coated panel are immersed in a 1 per cent solution of Rinso at 185° F. (85.0° C.). After 24 hours, the finish must be unaffected by the soap.

### Subtropical Exposure Testing

The first scientific data on the sun climate of South Florida were recorded in 1927. This was about six months before the first test panels were exposed. Continuous use of subtropical testing has been a valuable guide in the development of automotive finishes. Such subtropical tests can be made at all times of the year. Almost all panels exposed in South Florida show the same types of failure that are shown by the same finishes in other parts of the country. The information is obtained in much less time, usually one-half to one-fifth of the time required to obtain pertinent information in northern tests.

There are only a few months, during the summer, in which weathering tests can be made on panels exposed in the north. Even under the most favorable conditions, there are wide variations during these few months. If the finish is durable enough to be considered at all, the test must be started in the spring or must run over into the fall.

The subtropical tests are available throughout the year. There is never much variation from "summer values." This continuousness is shown in the following table of daily averages:

		SUNSHINE	VALUABLE ULTRAVIOLET
January to April	Miami	7.5 hours	5.5 hours
	Chicago	5.9 hours	(see note)
May to August	Miami	8.8 hours	5.9 hours
	Chicago	10.2 hours	3.5 hours
September to December	Miami	7.0 hours	4.5 hours
	Chicago	6.0 hours	(see note)

*Note.* Except in May, June, July, and August, there is little or no ultraviolet in the Chicago sunshine.

The usual exposure for test panels is at 45° inclination and facing south. Figure 1 shows that the sun impulse for such surfaces is at a very constant and high value throughout the year. It is easily seen why such panels undergo accelerated weathering when this curve for south 45° at Miami is compared with the curves of Fig. 2 for the northern latitudes.

Thus the value of subtropical tests rests on (1) constancy of sun impulse, (2) continuous "summer values" at all times, (3) the results being in excellent accord with the durability shown in actual use of the finishes (that is, the results of these subtropical tests do not show wide variation from actual durability in use, a variation which is common in other accelerated tests).

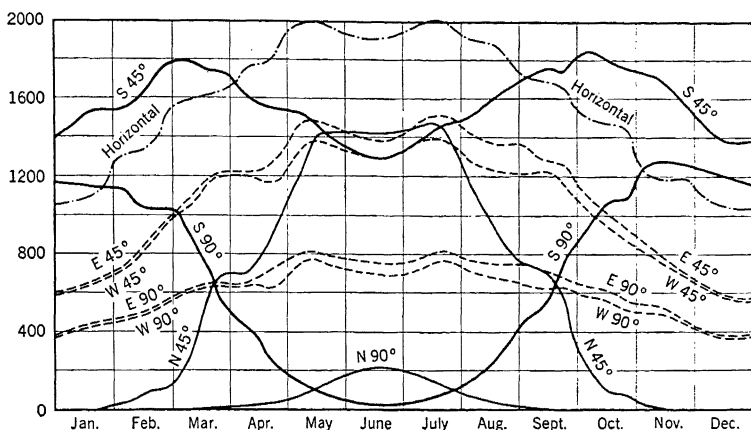
As a further explanation of this procedure, we are presenting herewith a discussion before the Rotary Club of Miami by Dr. O. J. Sieplein:

In Figs. 1 and 2, the curve marked "horizontal" shows the intensity of sunshine received on a horizontal surface throughout the year. This intensity is measured in terms of heat—British thermal units, B.T.U. One B.T.U. will heat one pound of water one degree F.; to heat one gallon of water from room temperature, 68°, to boiling requires 1,200 B.T.U.

The values in Fig. 1 are those determined by the Miami Sun-Ray Research.

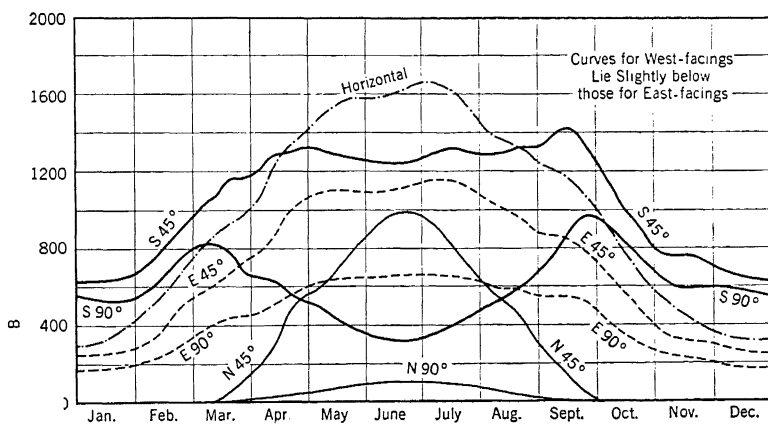
The U. S. Weather Bureau records sunshine intensity at less than ten stations in the country. Of these, Chicago (42° L.), New York and Pittsburgh (41° L.)

were chosen as representing the eastern industrial section of the country. An average of the normal values of the three stations is the curve for horizontal surface in Fig. 2—42° north latitude.



Sun Energy Received on Various Surfaces at Miami, Fla., 25°48' N. Lat.

FIG. 1.



Sun Energy Received on Various Surfaces at 42°N. Lat.

FIG. 2.

The direction and altitude of the sun change continuously during the day. When the angle of the sun's rays to the horizontal surface is known, it is possible to calculate the angle of the rays to vertical and inclined surfaces faced in various directions. These angles may be measured with a heliodon. This knowledge of angles permits the calculation of the intensity of the sunshine as shown



by the curves in Figs. 1 and 2—curves for the values for vertical ( $90^\circ$ ) and inclined ( $45^\circ$ ) surfaces facing the four cardinal points of the compass.

Sunshine intensity to vertical and inclined surfaces is calculated from the intensity and sun angle for horizontal surface and the sun angle for such other surface. Figures 1 and 2 show curves for the values for vertical— $90^\circ$  and inclined— $45^\circ$ —surfaces facing to the four cardinal points of the compass.

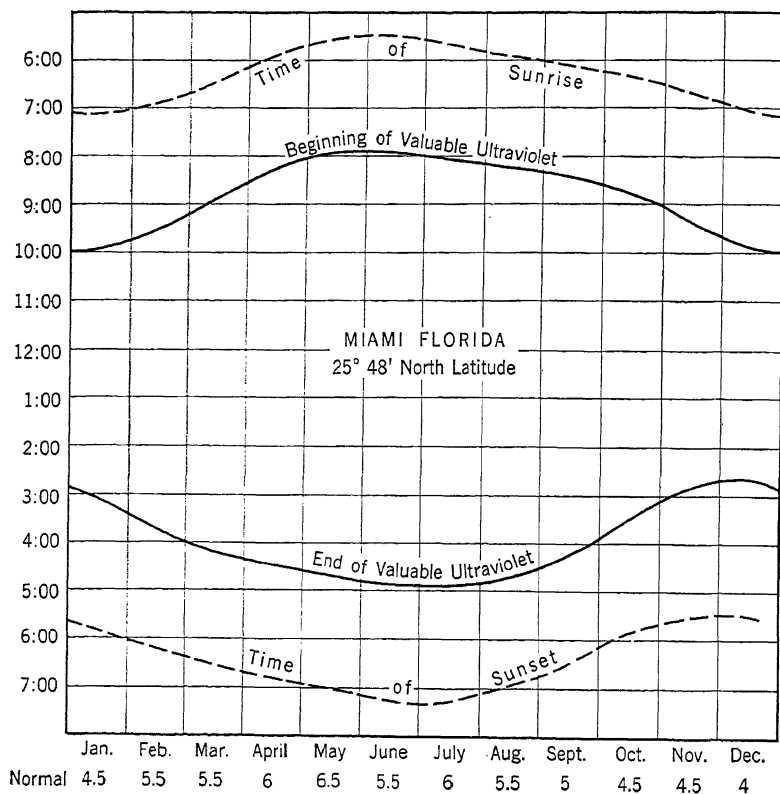


FIG. 3.

Practically all stations of the U. S. Weather Bureau record greater cloudiness after noon than before noon. This afternoon cloudiness causes some decrease in sun intensity, but causes a marked decrease in ultra-violet. Records of the Miami Sun-Ray Research show that 52% of the day's sun energy is received before noon, 48% after noon. These records also show that 60% of the day's ultra-violet is received before noon, 40% after noon.

The horizontal surface and all surfaces faced north or south are exposed for equal periods before and after solar noon. Inclined surfaces, however, differ. Those facing east receive sunshine between sunrise and sometime after solar noon, varying with latitude and time of year. For Miami, such surfaces receive 80%

of their sun dosage before noon in the summer and 85% before noon in the winter. At latitude  $42^{\circ}$ , the summer value is 82% and the winter value 90%.

Theoretically, the morning values of sunshine received by east-faced surfaces are the afternoon values for west-faced surfaces, and vice versa; but there is a difference between the actual sun dosage received by east facings and west facings, because of the greater afternoon cloudiness. Obviously, the cloudiness causes west facings to receive much less ultra-violet than east facings.

With the exception of the south vertical surface, which is present on the south wall of a home, the Miami curves lie higher, show much more sunshine, and vary less during the year than those for latitude  $42^{\circ}$ .

At both locations, north vertical surfaces get a small amount of sun during the summer half of the year. Vertical surfaces facing east, west, and south, and inclined surfaces facing north, east, and west, receive one-half to two-thirds of the sun energy falling on the horizontal surface. Inclined surfaces facing south receive somewhat more sun energy than the horizontal surface.

A study of the charts will disclose other striking differences.

Figure 3 shows the times at which the sun is high enough to yield valuable ultra-violet, under cloudless sky conditions.

The values marked "NORMAL" indicate the probable number of hours of such ultra-violet for the average day of each month of the year.

The prevalence of clear skies during the winter months causes the NORMAL to be quite close to the total possible; for example, we may expect four hours of valuable ultra-violet per day in December, out of a total of less than five hours during which the sun is high enough to yield such radiation. The floating cloud-masses, characteristic of the summer skies in Miami, reduce the NORMAL to a smaller fraction of the total possible; for example, the average July day has six hours of valuable ultra-violet out of a possible of nearly nine hours.

The same factors which make for this striking tendency to uniformity in the duration of ultra-violet, day by day throughout the year, also make for the same kind of uniformity as to the intensity of the ultra-violet during each day and throughout the year.

Figures 1 and 2 indicate total sunshine, containing heat, light, and ultra-violet. Figure 3 indicates the ultra-violet only. The comfort of heat, the desirability of light have long been understood. Recently ultra-violet has been recognized as the all important, the health giving factor in sunshine. The ultra-violet contained in Miami's sunshine in winter is recorded as being equal to or greater than the ultra-violet recorded in Northern locations, outside of city smokes, in June.

#### ACKNOWLEDGMENTS

The author is indebted to the Parker Rust Proof Company, to the Fisher Body Corporation, to the Chrysler Corporation, and to Dr. O. J. Sieplein for their helpful cooperation.

The author acknowledges particularly the assistance of Mr. S. G. Saunders and Mr. R. P. Jones of the Chrysler Corporation, Mr. Earl H. Quick of the Fisher Body Corporation, Mr. Henry H. Nelson of the Sharples Solvents Corporation, and Messrs. George A. Tracy, H. Dale Thieben, Vincent Connor, and Albert C. Litterst of his own staff.



## CHAPTER 15

### CASEIN PAINTS

ROBERT S. RADCLIFFE

#### History

How long the proteins of milk have been used as a binder for surface coatings is unknown. It has been reported (57) that early Hebrew texts gave instructions to the women of the community to save their curds for the coming of the itinerant painter in the autumn. He mixed his colors with these curds and decorated the homes of the community. For years it has been known that the addition of milk to "whitewash" improved its durability as well as its ease of application. The U. S. Patent Office issued patent 50,068 to Darwin P. Flinn in 1865, covering a paint of the following components:

White oxide of zinc, seventy-two pounds; fresh slaked lime, twelve pounds; resin, three pounds; milk, thirty-six quarts; linseed oil, six quarts, . . .

This patent describes one of the early attempts, in this country, to prepare a casein paint.

A year later, H. A. and D. E. Longsdorf patented (39) an "improved paint" composed of lime, casein, and alum, which were added to milk to brushing consistency. In 1867 Daniel R. Prindle patented (48) a "whitewash" made from lime, skimmed milk, and chrome yellow or other pigment. Again Hohenstein (31) and Munson (44) patented similar materials in 1885 and 1887, respectively. In 1896, Hall patented (24) a dry casein paint consisting of 50 per cent talc, 40 per cent whiting, and 10 per cent adhesive. The adhesive consisted of 60 per cent dry casein and 40 per cent "good, dry, slaked, and powdered lime." A number of modifications of the dry casein paint of Hall were patented in years immediately following its appearance. At the same time, a number of investigators had been preparing casein solutions for various uses and applications, such as casein varnish, paper size, and casein paints. With the patenting by Regnier (49) in 1924 of a

casein solution, made by the use of sodium fluoride, and further developments by Atwood (5) and others, the modern casein "paste-paint" came into existence.

The past forty years have therefore seen the development of modern casein paints. The Chicago World's Fair of 1933 and 1934 and the New York World's Fair of 1939 added impetus to their further development because of the unusual color effects produced by their use on the buildings of the Fairs. In Europe national trade barriers and policies have encouraged their development as substitutes for oleoresinous paints in those countries forced to import drying oils and resins. The recent years of business depression in the United States have also led to greater consideration of casein paints, because of their relatively low cost per unit of hiding power.

### The Casein Paint Industry

The Bureau of Census of the Department of Commerce released (12) in February, 1938, a comprehensive review of the manufacture of casein paints in the United States for the year 1937. This report and the reports of the Bureau for the years following presented figures sufficiently divided and complete to allow a very interesting analysis of the size of the industry and its growth and also to indicate the consuming public's preferences for certain types of casein paint. A part of these reports is given here.

TYPE OF PAINT	DOLLAR VALUE OF CASEIN-BOUND PAINTS			
	1937	1938	1939	1940
Cold water paints				
Exterior (paste or dry powder) . . .	238,840	235,309	261,412	213,691
Interior . . . . .	1,599,907	2,683,463	3,265,323	3,637,022
Dry powder form . . . . .	480,802	863,265	991,649	1,109,590
Total . . . . .	2,319,549	3,782,037	4,518,384	4,960,303
Plastic paints				
(Casein-bound) . . . . .	384,718	360,819	333,191	*
Calcimine . . . . .	3,364,066	3,077,748	3,023,098	2,543,269

\* These figures discontinued with 1940 tabulation.

Manufacturers also reported that in 1940 they produced 3,468,419 gallons of paste and semi-paste forms of paint and 14,975,532 pounds of dry powder paint for interior use.

These figures point out that the major portion of all casein paints manufactured are designed for interior walls and surfaces.

### Preparation of Commercial Casein

Casein, the phosphoprotein of milk, is precipitated when unpasteurized skimmed milk is treated with dilute acids such as lactic, sulfuric, or hydrochloric. The lactic acid may be produced by the action of bacteria on milk sugar. In this case, the casein is said to be precipitated by "self-souring." Rennet may be used also as precipitant. However, the protein precipitated in this manner, though of identical composition, has slightly different properties and is not used in casein paints, though some investigators (8) feel that it may be used to advantage.

The acid precipitation of casein is carried out by a number of commercial processes (9, 11, 60). The name of the acid used for precipitation designates the type of casein. Thus "muriatic," "sulfuric," and "lactic" caseins are available. Production records for the United States for the year 1934 (7) show that seven types were produced. The uniformity of the hydrochloric acid type has increased its popularity. After precipitation, the curd is washed, dried, and ground, and appears in commerce as a dry, white, sweet-smelling powder which can be kept, with reasonable care, for comparatively long periods of time. Commercially, casein is graded by the fineness to which it is ground. Thus 30-mesh, 80-mesh, and 100-mesh products are sold. Broadly speaking, the method of manufacture has little effect on the chemical characteristics of the casein produced. The principal factor governing the quality of the commercial product is the degree of care and chemical control maintained in its manufacture. Grades of casein manufactured by highly controlled processes are generally more uniform and command premium prices. A large distributor of casein gives the following analysis of standard and premium grades.

	STANDARD GRADE	PREMIUM GRADE
Ash .....	3.00%	2.00%
Total acid (ml. <i>N</i> /10 NaOH) ....	10.50	8.50
Free acid (ml. <i>N</i> /10 NaOH) ....	1.50	1.00
Fat .....	1.00	0.75
Solubility .....	99.75	99.90
Insoluble .....	0.25	0.10

### Chemistry of Casein

Because elementary chemical analyses of samples of casein produced in a number of ways and from various types of milk were in good agreement, it was felt for a number of years that casein was a pure

chemical compound. Work in the past decade has shed much light on its structure, and it is highly questionable whether or not it is a true chemical compound (57, 58, 59). It does exhibit, however, chemical reactions which are characteristic and follows general stoichiometric relations so that for many practical purposes it may be considered a chemical identity. It has been established as a complex compound, produced by the conjugation of amino acids. Because of its structure it is amphoteric and acts either as an acid or as a base. Its acid characteristics are the more prominent, so that as an acid it is strong enough to displace carbon dioxide from calcium carbonate.

Casein is practically insoluble in water, particularly at its isoelectric point ( $pH$  4.6). It is also insoluble in ordinary organic solvents, including alcohol and ether. It is readily soluble, however, in dilute solutions of the hydroxides of the alkali and alkaline earth metals as well as in dilute solutions of their soluble carbonates and bicarbonates. It is also soluble in 1 per cent solutions of sodium, potassium, and ammonium fluorides. Dilute solutions of alkali oxalates and alkali sulfides also act as solvents. Weak solutions of borax also dissolve casein.

Whether or not casein enters solution in the true sense is obviously questionable (57, 58). From the practical paint manufacturer's point of view it can be said that a workable paint vehicle may be produced from it by the use of the alkali and alkaline earth hydroxides and certain neutral, acidic, or basic salts. Proteins as a class are decomposed or hydrolyzed by high concentrations of either acidic or basic materials. It is essential, therefore, that casein be put into solution or suspension under controlled conditions of  $pH$  and temperature. The usual practice is to dissolve casein at  $pH$  concentrations of 5.0 to as high as 10.5 at controlled working temperatures. This is particularly true if the casein vehicle is to remain stable for considerable periods of time. If a casein paint is to be used shortly after its vehicle is prepared, control of strength of the solution materials is not of great importance. However, when permanent solutions are required, as in the production of casein paste paints, such control is essential.

Solutions of casein made by the use of alkali metal or ammonium hydroxide or salts maintain their properties more readily than solutions made from alkaline earth hydroxides or salts. This is due to the strong precipitating or insolubilizing action of the alkaline earths. Thus sodium hydroxide may be used to dissolve casein, but an excess will not cause precipitation. With lime, the casein is also dissolved, but when an excess is added the casein is precipitated from solution.

Likewise, paint films of casein laid down from alkali solutions are more easily penetrated by water than those laid down from alkaline earth solutions.

Casein also reacts with formaldehyde and similar compounds, in a manner which may be classified as a condensation reaction, to form a hard bonelike compound highly resistant to water. This reaction was employed in the application and hardening of casein paints in the past but has of late become of less importance.

As a dry powder, casein can be kept for long periods of time if stored with reasonable care. Water solutions, however, when allowed to stand exposed to air, are attacked by bacterial and mold growths which cause decomposition and putrefaction. It is essential, therefore, to include in casein paints which are to be kept in a liquid state for even short periods of time an ingredient which will prevent decomposition by bacteria and mold.

### **Types of Casein Paints**

The simplest type of casein paint was described by Hall (24) as a mixture of a pigment, as talc, and a binder, as dry casein and lime. This mixture was added to water until a satisfactory consistency for application was obtained. This simple composition is the fundamental basis for one general type of casein paint, namely, the "dry-powder" paint.

As previously pointed out, casein solutions prepared by Regnier (49) and Atwood (5) introduced the second type of casein paint, the casein "paste-paint." Such solutions had sufficient stability on aging that a liquid or plastic paint could be produced, with proper pigmentation. Because such solutions were, generally, neither excessively acid nor basic in nature, they could be packaged satisfactorily and thus could be sold as liquid or plastic paints.

It will be noted that in Flinn's early patent he used as binder not only milk but also a resin. Additions of resins, drying oils, waxes, and other similar binding materials to casein paints have been made in an attempt to improve durability, application, and film properties. Atwood (6) recognized paints having both casein and oleoresinous materials as binders as "oleocasein" paints. As a class oleocasein paints are not as readily defined as casein paste paints or dry powder paints, but they represent a considerable proportion of the commercial paints made with casein and therefore should be considered in all discussions of casein paints.



Casein is also used as a protective colloid for the preparation of emulsions. In the past few years, the so-called emulsion paint has appeared in the industry. These paints consist for the most part of a resinous or oleoresinous binder emulsified or dissolved in water. Casein quite often is used as the emulsifying agent or stabilizer in such paints. As the quantity of casein used in such paints is relatively small, emulsion paints represent but a small field for the use of casein in protective coatings.

In addition, there has been developed a type of paint which is known as "plastic" or "texture" paint. Such coatings are applied to new or old walls in heavy coats, generally with a trowel or similar applicator. This type of paint also may use casein as its binding medium. In Europe, particularly in England, the word "distemper" is used indiscriminately to describe any paint using water as a part of its vehicle. Such paints include the various types of casein paint discussed here, as well as paints using glue as a binder. Because of the looseness of the term distemper, it will be avoided. Lastly, dry casein paints may be confused with "calcimine." Formerly such products were made using glue as a binder. Such materials many times use casein as binder, at least in part, and may be considered as a form of dry powder paint.

### Formulation of Dry Powder Paints

The development of the formulating practice of casein paints of the dry powder type in the United States can readily be followed by reviewing the patent literature on the subject. Hall's patent (24) of 1896, previously mentioned, presents the simplest dry powder paint, consisting of pigment, casein, and lime. In 1899, he patented (26) a paper sizing in which he dissolved casein in an alkali and added boric acid to get better solubility. It was also claimed that the boric acid would induce a preservative action. A year later he patented a calcimine (27) in which he included a percentage of dry, powdered sea moss to induce thicker consistency in the paint, increase its ease of application, and produce a more uniform paint film. In this product he used a combination of borax and sodium carbonate to dissolve the casein. These patents were followed by others, which included a paper size using calcium sulfate as a part of the pigment to decrease the solubility of the size (29) and a casein solution made with hydrochloric acid casein and trisodium phosphate (28). By the use of the phosphate he obtained a solution of thinner consistency.

Adams (1) added alum to obtain a bodying action. Govers (22) prepared a slightly acid coating with improved flow and less tendency to decomposition by the use of sodium phosphate and sodium thiosulfate. He claimed that the use of thiosulfate also decreased the tendency of the size to foam during its incorporation with water. Dunham (15) pointed out that casein dissolved in the presence of alkali oxalates produced a solution of much thinner consistency. In other words, less water was necessary to prepare a solution of a given consistency if such oxalates were present. Schwartz (56) used sodium metaphosphate to increase the length of time which a casein paint based on lime as the alkali could be used without coagulation. Isaacs (35) used a combination of lime, sodium fluoride, and sodium silicate to dissolve casein; Lützkendorf (37) used a combination of sodium silicate and sodium hydroxide.

In dry powder casein paints there has not been any great tendency to include waxes, drying oils, or resins with casein as a part of the binder of the paint. S. S. and Benjamin Ruston (50, 51) prepared dry powder paints by an ingenious combination of resin, sodium carbonate, lime, and aluminum sulfate with casein, and drying oil, sodium carbonate, lime, and zinc sulfate with casein. Many formulators have recognized (22, 54, 55, 56) the value of such additions to this type of casein paint after the powder was added to water. U. S. Federal Specifications (17) for such paints suggest such an addition.\*

Therefore, the general composition of the binder of dry powder casein paints consists mainly of casein and lime, modified by other alkalies, salts, or other compounds to improve certain characteristics of the paint.

There has been some discussion as to the type and amount of lime to use for best results. M. D. Schwartz has been quoted (57) as stating that the ratio of CaO to casein should be as 87.5 pounds to 100 pounds. He determined the amount of CaO available to the casein by reaction of the lime with a hot solution of cane sugar. Bryson (8) showed that the use of hydrated lime, essentially 100 per cent  $\text{Ca}(\text{OH})_2$ , gave paints of greater durability than lime carrying impurities, especially if the impurity was  $\text{Mg}(\text{OH})_2$ . It has been found

\* In March, 1940, Federal Specifications for Paint: Cold Water, Casein-Binder, Light Tints and White TT-P-23 was superseded by specification TT-P-23a. This new specification discards for the most part all constituent requirements of the older specification and demands certain performance requirements, particularly as to color, hiding power, and washability. Since the older specifications have an academic interest they are referred to at various points in our paper.

essential that the lime or other dissolving chemicals be incorporated in sufficient quantity to produce solution of all the casein without excess to cause precipitation or brittle films. Undissolved casein will induce coarseness or poor texture in the paint film.

Early dry powder paints carried as pigments those materials which are known in the oleoresinous paint field as extenders or inerts. Among the pigments were whiting, chalk, talc, magnesium silicate, blanc fixe, and china clay. Allen (2) introduced flake mica to improve the elasticity of the film. Mica has been said also to improve the brushing of such paints. These materials gave sufficient hiding power when the paint film was dry but in the wet film were often so transparent as to be unsatisfactory (55). In recent years, the incorporation of higher hiding power pigments has become general practice. These include zinc oxide, lithopone, zinc sulfide, titanium barium pigment, and titanium dioxide. Former federal specifications (17) required 15 per cent by weight of zinc sulfide or 13 per cent titanium dioxide, as pure or extended pigments, for one grade of dry powder paint. All pigments or dry colors used for dry powder paints containing lime must of necessity be limeproof or unreactive to lime in dry form or in solution. This limits the colors available to materials, such as earth colors, cadmium reds and yellows, iron oxide colors, and the like. Poor dispersion of pigments in casein paints produces an unsatisfactory paint film, particularly when such pigments or colors are of high hiding power or tinting strength. If the pigments are poorly dispersed the film contains small aggregates of pigment particles which show up as brilliant spots in the film. To avoid such variations, many pigment manufacturers are marketing pigments which disperse readily in water.

The quantity of casein needed for binder naturally varies. Hadert (23) claims that paints can be made with as little as 3 per cent and with as much as 15 per cent by weight on a dry basis. Early dry powder paints carried 5 to 7 per cent casein, but modern requirements demand casein contents in the range of 8 to 12 per cent. Scholz points out, however, that concentrations of casein above 10 per cent cause hard brushing unless special care and materials are used in dissolving the casein (54, 55). It is evident that the amount of binder required is dependent on the adhesive quality of the binder, on the ratio of pigment volume to binder volume, and on surface character of the pigments used (8).

Most dry powder paints depend on the use of alkaline earth hydroxides or salts in excess to produce an insoluble film. In 1892, Hall

patented a process for coating materials in which he hardened casein films with formaldehyde (25). To a composition of 80 per cent pigment and 20 per cent casein he used  $3\frac{1}{2}$  per cent of a 40 per cent solution of formaldehyde. Similarly Dunham used hexamethylene tetramine (14). Chromates and dichromates have also been suggested (55). There also sprang up among painters the practice of treating the dried casein paint film with a solution of formaldehyde to harden it and render the casein insoluble.

The use of compounds to prevent decomposition by bacteria or mold growth is not as prevalent in dry powder paints as in paste paints. This is due largely to the fact that dry powder paints are not exposed in liquid form to the air for extended periods of time. Generally, enough powder is mixed with water to suffice for the day's painting and, at most, the paint is not kept for more than a few days after being prepared. However, many dry powder paints carry preservatives in the interest of safety. Federal specifications require that dry powder paints must be made so that after dilution they can stand for eighteen hours without giving off an offensive odor.

### Casein Paste Paints

The production of a casein-bound paint in the liquid form was dependent on the production of a casein solution that would remain stable over extended periods of time. To do this, it was necessary that solution of the casein be effected by alkalis which would not cause precipitation if present in excess. Preservatives to prevent the decomposition of the paint by mold or bacteria growth became a necessary ingredient in such solutions. To produce a satisfactory paint, the casein solution, in addition, was required to bind sufficient pigment for adequate hiding power, produce a durable and pleasing paint film, be reasonably easy to apply to a given surface, and maintain the pigment in suspension for an adequate length of time.

The obviously simply method of preparing such casein solutions was to dissolve casein in hydroxides, or salts of weak acids, of the alkali metals or ammonia. One of the first patented paints of this type used ammonia as the solvent for casein (21). Unquestionably, other simple solutions of casein of this sort are the basis of many of the casein paste paints on the market. Such casein solutions are of necessity caustic in nature. This alkalinity is disadvantageous because it limits the types of packages in which the paints may be distributed and the types of pigments with which they may be pigmented, and because of its effect on the skin of the person applying them.

Regnier (49) prepared a casein solution which showed an acid reaction by using sodium fluoride as the means of solution. Using 100 pounds of hydrochloric acid precipitated casein, 8 to 16 pounds of sodium fluoride, and 400 pounds of water, he prepared a casein solution which was sufficiently acid so that colors which would be attacked by alkaline solutions could be used. He claimed that the viscosity of the solution was dependent on the amount of water used. He pointed out that by adding trisodium phosphate or ammonium oxalate he could improve the flowing qualities of his solution. He also recommended that the solution be made at a temperature of about 160° F.

It remained for Atwood (5) to produce a casein solution which was essentially neutral. This solution was described in its patent as ". . . a thick, viscous casein solution characterized by its stability and uniform viscosity over long periods of time and comprising the product resulting from swelling casein by means of a swelling agent as sodium fluoride in the presence of water and at an elevated temperature, and dissolving the swollen casein in the manner such as to produce a thick, viscous casein solution having pH values within the limits of 4.6 and 7.0. . . ." Atwood disclosed the following procedure for the preparation of his solution: 55 pounds of casein were soaked in 30 gallons of water at 150–160° F. To this were added 5 pounds of sodium fluoride and 2 pounds of ammonium chloride. After complete swelling had been effected, 6 pounds of borax were added to dissolve the casein to a thick gel-like solution. He also noted that a strong alkali, such as sodium hydroxide or carbonate, could be used for solution, but when used it would be necessary to neutralize the alkali with boric acid.

Iddings (32) produced a casein solution by peptizing with soluble fluorides in the presence of active silicates or silica. He described a method requiring 100 parts of casein, 150 parts of water, 14 parts of sodium fluoride, 5 parts of ammonium fluoride, and 7 parts of pulverized silica. The solution was carried out at 195° F. and had a pH of 6.9–7.0 when sulfuric acid precipitated casein was used. Iddings also added to similar solutions such compounds as acetone, butanol, diethylene glycol monoethyl ether, ethyl acetate, ethylene glycol monobutyl ether, isopropanol, and cyclohexanol to impart flow and, in the cases of the high boiling compounds, to act as plasticizers of the casein film (34). These compounds were added in amounts of about 2 to 5 per cent on the basis of the casein solution which carried about 17 per cent casein.

**Preservatives for Casein Solutions** As has been pointed out, the advent of the liquid casein paint was not assured until preservatives had been developed to insure against deterioration of the solution by mold or bacterial growth. The literature of casein paints is saturated with details on the use of a great number of materials for this purpose. The manufacturers of casein paints have gone a long way in the solution of this problem, but it remains one which is not completely solved, owing obviously to the many kinds and sources of such growths and the many conditions of exposure of the paint or the paint film. Space does not allow any more than the mere mention of some of the compounds that have been used. Hall (26) stated that borax would prevent deterioration of casein solutions. Scholz (54) disclosed that in casein paints carrying lime, borax tends to confine the mold growth to those of the white or light pink or orange-colored varieties. He claimed that the addition of tribromophenol to such paints practically eliminated such growths. He also stated that such compounds as sodium trichlorophenate and parachlorometacresol can be used similarly (55).

Sodium and ammonium fluorides in themselves are good preservatives. Corrosive sublimate has been suggested as the best all-round preservative (57). The same source stated that zinc sulfate may be used to advantage but that it embrittles the film. Thymol has been suggested (30) as has been chloroisocthyrmol (30). It has also been stated that sodium salicylate and salicylic acid (45) have been used in the industry. Recently such compounds as sodium orthophenylphenate and sodium 2-4-5 trichlorophenate have been suggested as of value as preservatives (13). Phenol has been used widely but its odor must be masked by some material such as pine oil, which in itself may be found to have a minor preservative action.

**Formulating Casein Paste Paints.** The pigmentation of casein paste paints has followed the trends of the dry powder paints. Early paste paints contained extender pigments for the most part. White pigments of higher hiding power were incorporated as the demand for higher hiding power and greater color brilliance increased with the increased popularity of such paints. More care was observed in the selection of pigments, both white and extender, for paste paints than for dry powder paints. Pigments were required which would in no way affect the stability of the casein solution. For example, pigments such as zinc oxide, which had an alkaline reaction, would have a tendency to induce instability in some casein solutions. Likewise, pigment manufacturers prepared pigments especially designed to dis-

perse easily in water or casein solution, improve the flow of the products into which they were introduced, improve the brushing of the paints, and decrease the amount of settling of the pigment. The range of dry colors that was made available for use in casein paints was widened by the advent of the paste type paint. Since these paints did not carry lime or an excessive amount of alkali, many colors which were unsuited for dry powder paints because of their lack of fastness to lime could be used in paste paints. Manufacturers learned to consider any color as available to them if it held up in their casein solutions. As a consequence, the public was introduced to a wide range of brilliant and vivid colors which previously had not been associated with casein paints.

In addition to casein solution, pigment, and preservative, the formulator of casein paste paints included other materials to improve the working qualities of his paint. The common casein solution did not produce a paint of entirely satisfactory application and film characteristics. In addition, settling or severe caking of the pigment had to be overcome when certain solutions were used. To eliminate such difficulties, it became common practice to include materials in the formula which would develop a "false body" or a greater yield value in the paint. Hall recognized this need when he incorporated sea moss into his simple "calcimine" (27). Again, Adams (1) included alum in a similar compound for the same purpose. Goodell and Tarr (21) used a wax emulsion. Hadert (23) indicated a rather wide use of starches and dextrin in dry powder paints. Other water-soluble gums or gel-forming materials such as gum tragacanth, agar-agar, and various soaps were used. However, the simple method of incorporating emulsified drying oils, varnishes, or resin solutions presented to the casein paint formulator the most satisfactory method of overcoming these weaknesses of casein paints. The addition of these components improved at the same time the water resistance of the coating. The incorporation of such oleoresinous binders in casein paints led to the development of "oleocasein paints."

### Oleocasein Paints

It has been observed previously that the film laid down by dry powder paint will become insoluble in water due to the action of the excess lime that is present in the paint. A film from a casein "paste paint" will be more or less soluble, because the film is derived from a solution of casein which contains no hardening agent. Consequently, casein paints which are to withstand washing with water must be

derived from dry powder paints or be hardened by washing with such compounds as formaldehyde. The latter treatment destroys one of the advantages of the paste paint because it introduces a disagreeable odor during painting. It is only reasonable, therefore, to expect that formulators of casein paste paints should attempt to improve their resistance to water by incorporating into such paints drying oils, gums, resins, or waxes.

The extent to which casein paints have been modified to "oleocasein" paints cannot be definitely established because manufacturers have been reticent about distributing information on the art of their formulation. Atwood (6) implied that most quality casein paste paints have some binder other than casein. Hadert (23) and Bryson (8) have enumerated many modifying binders that have been used. Iddings (33) has patented a casein solution in which is incorporated a glycerol-phthalate resin. Magill and Dangelmajer (40) have disclosed the solution of casein through the use of formamide and the incorporation of rubber latex into the coating.

The incorporation of modifying materials such as drying oils and resins in casein paints widens tremendously the field of such paints and, at the same time, enlarges the number of problems which must be solved by the manufacturer and formulator before a marketable product can be prepared. Because of the comparatively recent popularity of such paints, the technology of their formulation is proceeding at such rapid strides that the fundamentals of formulation are not as yet established. The literature discloses a vast number of compounds and proprietary materials which have been said to give good results. To discuss these compounds in detail is beyond the scope of this work. The essential operation of their incorporation is emulsification, either by reaction of their organic acid components with alkali or by the use of such emulsifying agents as soap, triethanolamine, or like materials. Oleocasein paints are an attempt to produce paints from water solution or suspension, which will equal in durability and application characteristic paints made in organic solvents. As has been shown previously, the sales of casein paste paints indicate that such paints have a place in the protective coatings field.

### Casein in "Emulsion Paints"

The distinction between oleocasein paints and emulsion paints carrying casein is not clear-cut. Oleocasein paints may, in the last analysis, be classified as emulsion paints, in that they generally contain the oleoresinous part of the binder in some form of emulsion. In this



discussion, an emulsion paint is considered to be one in which the binder is essentially oleoresinous. Casein is incorporated in such paints not for its binding qualities but as a protective colloid or emulsifying agent for emulsification of the oleoresinous binder in water. As an example of a typical emulsion paint, Ott and Breyer patented (46) in Germany a water paint which had as its binder a glycerol-phthalic anhydride-linseed oil acids reaction product emulsified in water containing casein, ammonia, and borax. A similar French product is obtained by mixing ammoniacal solutions of natural or synthetic resins and casein and neutralizing the excess ammonia with drying oil (19). An American manufacturer has suggested the production of an emulsion paint by emulsifying alkyd resins, either of the fluid type or in solution in organic solvents, with casein (47). In this formula, 70 parts of casein by weight are used for each 1,000 parts of resin.

Emulsion paints are just beginning to appear on the American market, though in Europe they are being looked on with considerable favor. This is particularly true in those countries where national policy or lack of natural resources restricts the use of drying oils and even casein for paints. Several American resin manufacturers have made available to the paint manufacturer similar water suspensions, particularly of the alkyd type. What part casein will play in such products is, of course, not as yet established. With the advent of emulsion paints, in which the binder is almost exclusively oleoresinous, a further step has been taken toward the goal of making a paint with water solution which will be equal to that made with organic solvents.

### Characteristics of Casein Paint Films

A paint has been described as "a mixture of pigment with vehicle, intended to be spread in thin coats (films) for decoration or protection or both" (3). Students of the pictorial arts have pointed out that the emphasis placed on the primary purpose of the use of paint—whether it is for decoration or for protection—varies in concordance with the periods of artistic development and artistic depression. In recent years a period of artistic development has occurred in this country and the emphasis has been placed on the decorative value of paint, rather than on its protective value. Homes, office buildings, and manufacturing establishments have been painted with a thought to protection of course, but with more thought to the improvement of the appearance of the structures. Homes were formerly painted primarily for protection, whereas now a house paint must give a pleasing appearance throughout its life as well as adequate protection from the ele-

ments. Because casein paints employ water as the solvent for the binder and because they require some period of hardening before they show any resistance to weathering, they have not been used widely for exterior paints or paints which would be subjected to severe washing or abrasion. The decorative values of casein-bound paints have been appreciated in recent years and their popularity with the public has increased despite their lack of durability. In addition, technicians working in the field have improved the durability of casein paints, particularly the "oleocasein" type, without materially lowering their decorative values, so that new more durable casein paints are appearing on the market.

However, there are some fundamental limitations governing the construction of casein paints which must be appreciated in order that one may understand their true place in the protective coating industry. These limitations tend also to circumscribe the uses to which these products may be put. The restrictions which govern casein paint formulation are likewise those which bring to these paints some of their outstanding properties. Because many of the limits do not apply to oleoresinous paints, casein paints are at times at a disadvantage by comparison. A true appreciation of the limits of both types of paints rather than a comparison of their properties leaves the conviction that both types of paints have definite fields of use.

**Consideration of Pigment Volume.** In the construction of a paint formula, the relation of the volume of pigment to the volume of binder is of primary importance. This relation establishes in a general way the film characteristics of the paint. Thus, in oleoresinous paints, a high pigment volume and a low binder volume produce a flat paint (53). High relative binder content produces a paint with gloss or luster. High pigment concentration tends to increase the hiding power of the paint (52, 53). Since hiding power is dependent on the difference in indices of refraction of the pigment and its surrounding media, the hiding power is increased because at high pigment concentrations a pigment-air interface, rather than a pigment-binder interface, is produced. At high pigment volumes, durability is poorer, within limits, and brushability may be materially hampered. There are of course other factors such as oil absorption of pigments, volatile content of the paint, the type and wetting power of the binder, and the physical condition of the pigment which affect film properties, but none of these is of as great importance as the pigment to binder volume relation.

Below is a table which may be used as a rough separation of oleo-resinous paints into types by pigment to binder ratio.

PIGMENT VOLUME	BINDER VOLUME	PER CENT PIGMENT VOLUME IN TOTAL SOLID VOLUME	TYPE OF PAINT
1.0	0.4	71.4	Flat—Poor durability
1.0	1.0	50.0	Flat to eggshell
1.0	2.0	33.3	House paint
1.0	3.0	25.0	House paint
1.0	1.25	44.5	Gloss paints
1.0	2.0 or higher	33.3 or less	Enamels

It has been pointed out previously that true casein paints may contain as little as 3 per cent by weight of casein and up to 15 per cent casein. Scholz has also pointed out (54) that it is very difficult to make casein paints of satisfactory application properties with casein contents of 15 per cent or higher by weight. A tabulation of a dry powder paint using 10 per cent by weight of casein as binder is given below:

	POUNDS	GALLONS
Lithopone (28% ZnS) . . . . .	53.6	1.496
Magnesium silicate . . . . .	18.4	0.774
China clay . . . . .	7.0	0.321
Lime $\text{Ca}(\text{OH})_2$ . . . . .	11.0	0.647
Casein . . . . .	10.0	0.955
Total . . . . .	100.0	4.193

It may be seen that this paint using 10 per cent casein by weight has a pigment volume of 77.2 per cent if the lime is considered pigment and 60.2 per cent if the lime is considered binder. This concentration of pigment places the paint in the class of flat finishes, without consideration as to whether or not the casein will form a continuous or lustrous film as it dries or hardens. True casein paints are therefore limited to the development of flat or matt finishes. Modification of casein paints with oil or resins allows for higher binder contents, but the drying of such materials in the presence of the water needed to dissolve the casein is not conducive to the production of a lustrous film even if the binder concentration is such as to allow the development of gloss. Casein paint formulas are generally confined to those which produce flat to eggshell films.

The restricting of casein paint formulas to those producing flat films limits the possible uses for such paints and allows them to find a definite place in the surface coating industry. In casein paints, pig-

ment hiding power efficiency is increased so that such paints have high hiding per unit of pigment cost. This high hiding power is conducive to lower painting costs, more brilliant and more permanent film colors, and, when a white base is tinted to pastel shades, cleaner and brighter tinted paints. Since casein does not discolor or "yellow" when its films are aged either in the daylight or in the dark, as do most oleo-resinous films, the permanence of the color of casein paint films is enhanced. The low binder content and the fact that the binder is not oily in nature tend to inhibit the collection of dirt and dust upon the paint film. The incorporation of oils and resins in casein paints tends to improve the durability of the paints but, with this increase in durability, hiding power, color brilliance, and permanency are decreased. Casein paints, therefore, are revealed as coatings which have low cost per unit of hiding power, are highly reflective to light, have bright and permanent decorative colors, and have limited durability. There are many places where such decorative paints may be used in preference to a more durable film.

**Durability of Casein Paints.** The preceding discussion implies that casein paints have limited durability; however, it must be emphasized that durability is a comparative value and the published information on the durability of such paints, particularly those formulated by modern technique, is indeed very meager. One investigator (8) feels that such paints, when hardened properly, have far more durability than has been attributed to them in the past. He bases this conclusion on limited exposure tests. When the designer of the Chicago "Century of Progress Fair" conceived the plan of buildings grouped as large areas of highly reflective and brilliant color, casein paints were selected for the painting of some buildings. This gave manufacturers and technicians the impetus necessary for the study of such coatings for exterior paints. Previously, paints made and hardened with lime were used on exterior surfaces as they had reasonable durability; paints made with alkali hydroxide or alkali salts were confined to use on interior surfaces. The advent of new processes of manufacture, new types of casein, and new modifying materials has brought wider use of casein paints as exterior coatings. There are now on the market several materials of the paste paint type which are suggested for exterior use.

As interior finishes, casein paints have been described as washable but not "scrubbable" (16). They require a period of aging to harden them before they will resist water and abrasion. The period of aging before washing that is generally suggested by manufacturers is thirty

days or longer. Tests have indicated that mold growth will attack casein paint film exposed in warm damp places. On the other hand, casein paints are less affected by free lime in new plaster walls than are oleoresinous paints.

### **Manufacture of Casein Paints**

Dry powder paint manufacture consists merely of a thorough mixing of the dry components of the paint. Care must be taken to maintain the materials in such condition that they can be thoroughly mixed with the equipment at hand. Hygroscopic materials must be avoided and the moisture content of all materials controlled. Dry grinding equipment is generally brought into use to insure a homogeneous mixture. The manufacture of casein paste paints follows generally the procedure used for the manufacture of oleoresinous paints. The casein solution is prepared in a container or kettle which, when the process of manufacture requires it, is heated—usually with steam. This solution is used immediately or set aside to be used as needed. In either event, it is placed in a mixer and the pigment and other ingredients added to it and mixed with it until a uniform paste is obtained. In the past, it was deemed unnecessary to disperse the pigments further by grinding. As the quality of casein paste paints improved it was found that dispersion by grinding was essential, and modern technique calls for grinding with equipment similar to that used in the oleoresinous field. Oleocasein paints and emulsion paints require more highly specialized equipment and procedures, because of the necessity for the development and maintenance of an emulsion. With such paints the order of addition of the ingredients and the type and amount of mixing and grinding are important factors. The manufacture of such paints is dependent on the formula involved, and general methods of manufacture cannot be given. There are of course many special procedures prevalent in factories for the manufacture of even the simplest casein paints. Some of these have been patented (41, 42).

### **Economics of Casein Paints**

It has been implied in this discussion of casein paints that such paints have comparatively poor durability, high decorative value, and low cost. The poor durability and a misunderstanding of their values have impeded the progress of casein paints. Because they were made in water solution they were associated with water paints, which used as the binding medium glue, which may have neither the strength nor the aging qualities of casein. Since such water paints generally sold at

lower prices than oleoresinous paints, casein paints inherited the name of "cheap paints." As Atwood (6) has so aptly pointed out, modern casein paints carry quality ingredients that belie this classification. The price of casein over a period of years has been very similar to that for which vegetable oils have been sold. New uses for casein have been found that may tend to maintain its cost at a higher level. Therefore, in comparing casein paints with oleoresinous paints from the point of view of cost it can be said that on the basis of decorative value or hiding power, casein paints are cheaper; on the basis of durability, oleoresinous paints are cheaper. With the rapid strides that are being made in casein paint technology, these conditions may not exist for long.

In this discussion, a great number of patents have been cited. With few exceptions there is scarcely a field in the coating industry that has been so well covered with patents as casein paints. Normally, in the paint industry, patents on finished products have not been prevalent. Many patents on dry powder paints have been cited and paste paints have been covered by patents since their inception, and are controlled by a patent license structure (4).

### Other Casein-Bound Coatings

The foregoing discussion of casein paints has dealt almost exclusively with these paints as used for the painting and decoration of buildings and other large surfaces. Casein-bound coatings, which, in the last analysis, may be considered paints, are used in many other fields. In certain of these fields the formulation and the use of such coatings are an art in themselves. We have previously mentioned the sizing of paper as one field where casein coatings are used. Here the casein coating is used to impregnate the paper as well as coat or decorate it. Casein-bound coatings are used for leather finishes and dressings and for finishing textiles (55). In these industries, casein is used in much the same way as in casein paints; however, the specific problems of manufacture are sufficient to develop a complete technology for the utilization of casein in each field. In fact, two-thirds of the casein produced in the United States is used in the paper industry (36).

Casein is used as binder for certain water colors and show card paints. They are more waterproof than similar products made with glue as the binder. Such materials may carry amounts of hygroscopic materials in order to avoid excessive hardening prior to use and to allow them to be worked up satisfactorily in water. These and regular commercial casein paints are used for advertising displays, posters,

and theatre scene painting. Cement or concrete paints are made with Portland cement and a casein binder (43). Casein has been suggested for roof coatings and cements with pitch and asphalt and for a coating with asphalt to impregnate fabrics and felts (38). Casein paints are used as undercoats in felt base linoleum floor coverings. A cement for fixing linoleum to floors uses casein, linseed oil fatty acids, and a phthalic anhydride condensation product (18). Casein varnishes have been patented for wood finishing (20) and for fixative for drawings (10).

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## CHAPTER 16

### ALPHA AND GAMMA PROTEINS FOR WATER PAINTS

WILLIAM J. O'BRIEN

#### ALPHA PROTEIN

##### History

Within the last five years a new raw material has been put on the market. This is an isolated protein from soybeans, known commercially as Alpha Protein. The product falls in the same general family of chemicals as casein. However, it differs chemically in that milk casein is a complex protein containing among other things a phosphorus group, whereas alpha protein would be classified as a simple protein consisting largely of glycinin. Generally speaking, alpha protein can be used where milk casein is used. Because of its somewhat different characteristics, however, it is more adaptable for certain other uses than milk casein.

The first commercial production of soybean protein in the United States was made in Chicago \* in 1935. The original plant was set up to manufacture 5 tons of isolated soybean protein per day. Unfortunately shortly after the plant was put in operation an explosion occurred which destroyed it completely. A new plant was built in 1936 on practically the site of the old one. It was designed in units of 5 tons each with an eventual total tonnage of 15 tons per day. At the present this plant is producing and selling approximately 15 tons of alpha protein per day.

##### Manufacture

The source of alpha protein is soybeans. The soybean contains

Protein .....	35-40%
Oil .....	18-20%
Moisture .....	10-11%
Carbohydrates .....	25-30%

The process for extracting alpha protein has two steps: (1) the preparation of meal or flakes and (2) the extraction of the protein.

\* By the Glidden Company.

In the manufacture of the flakes from the raw beans it is highly desirable that the meal be as free as possible from oil. It is also quite important that the meal be subjected to as low a temperature as possible. Protein is extremely sensitive to temperature and pressure variations. The process employed in securing proper meal therefore plays quite an important part in the subsequent steps of the operation.

It has been found that the best meal for protein extraction is obtained by the use of the solvent extraction process. The solvent used in this process is usually hexane, a mineral oil solvent, which has a boiling point of 155–158° F. (68–71° C.). The meal secured from the solvent extraction process will analyze approximately the following:

Protein .....	44.0%
Fat .....	5.0%
Fiber .....	7.0%
N.F.E. (Carbohydrate) .....	29.0%
Remainder—Extraneous matter such as cellulose, etc.	

Soya protein is largely composed of glycinin, which is soluble in a large variety of electrolytes. The essentials of the process for obtaining soya protein are to extract the protein from the soybean and free it from such materials existing in the soybean as cellular material, carbohydrates, and oil.

Latest evidence seems to point out that the protein existing in nature in the soybean has a very high molecular structure. The steps involved in extracting the protein therefore consist first of dissolving the protein and separating it in a soluble form from extraneous matter, such as cellulose. The second step necessitates the removal of carbohydrates, etc., which are water soluble. The third step involves the hydrolysis or reduction of the size of the molecule.

In the first step suitable electrolytes must be employed. Such electrolytes may be sodium chloride, sodium sulfite, sodium hydroxide, sulfuric acid, and hydrochloric acid. The nature of the electrolyte used plays quite an important part in the subsequent properties of the protein.

The second step, to remove carbohydrates, etc., necessitates the reprecipitation of the protein, filtration and removal of the soluble sugars, pentosans, etc.

The third step involves hydrolysis treatment. This step is carried out in such a manner as to control the physical characteristics of the

resulting product. Temperature, pH control, and other factors are very vital in this step.

It can be seen that the above procedure involves a great deal of equipment in processing when one considers that the weight of material handled per quantity of solution is relatively small. Certain other factors also enter in, such as the effect of enzymes present in the solution, bacteria, etc., which tend to change the physical and chemical properties of the protein. As a result of the above processes, 30-35 per cent of the protein based on the original weight of meal used can be obtained. The dried commercial product obtained will show this analysis:

Protein .....	96-97%
Ash .....	0.5% (maximum)
Crude fiber .....	0.5% (maximum)
Carbohydrates .....	2.0% (maximum)

### Uses

Alpha protein is now being used as the adhesive, film-forming, and waterproofing agent in cold water paste paints. The use of alpha protein in water paint is illustrated by the following typical formula:

1. Alpha protein .....	100 lb.
Water .....	400 lb.
2. Borax .....	15 lb.
Water .....	110 lb.
3. Dowicide "A" or phenol .....	6 lb.
Water .....	50 lb.
4. Diglycol laurate .....	5 lb.
5. Linseed oil containing 0.02% cobalt .....	35 lb.
6. Pine oil .....	7 lb.
7. Dowicide "A" .....	2 oz.
Locust bean gum .....	2.5 lb.
Water .....	50 lb.

Soak No. 1 for 10 minutes. Start heating with either live steam or steam-jacketed kettle under agitation. Add 2. Allow temperature to rise to 160° and hold between 160-170° until the protein is thoroughly cut. This can be determined by pouring some of the liquid over a clean plate glass and holding to the light. When the protein is thoroughly cut there will be no evidence of gelled particles. Sometimes there is a slight turbidity which can be ignored. Add 3, 4, 5, 6, and 7 in order, allowing approximately 5 minutes between each step and keeping temperature between 140-160°. Agitate solution for approximately 20 minutes and pass through colloid mill if possible. This step is not entirely necessary as satisfactory results can be obtained otherwise. Add approximately one-half the total protein solution in a change can mixer; then add the following pigments:

Lithopone .....	825 lb.
Whiting .....	110 lb.
Mineralite 3X .....	75 lb.

This will form a very heavy paste. Continue agitation until a thorough mix is obtained. Add remainder of the protein solution and continue agitation until pigments are properly dispersed. Grind with roller mill, having loose setting so as not to fracture the mineralite. This tends to cause discoloration.

Gum Tragacanth, Karaya Gum, or ammonium alginate may be used in place of locust bean gum. If ammonium alginate is used it is well to prepare the dispersion in a mechanical device such as the change can mixer by first adding one-half of the water and Dowicide "A." Then sprinkle in the alginate and agitate until heavy mass results. Add remainder of water. We recommend that 7 be added in the preparation of the paint, i.e., add half the protein solution to the change can mixer, then the specified amount of alginate dispersion, pigments, and remainder of clear protein solution.

This formulation will give a satisfactory water paint; it is one of a number that can be used and is illustrative of the general type.

Other uses might be mentioned:

As a protective colloid and thickener for latex emulsions.

As the adhesive in paper coatings and washable wallpaper coatings.

As a protective colloid in emulsions of rosins, oils, waxes, and gums. Because of its excellent properties in this direction it is widely used in the sizing of paper, the so-called Prosize \* treatment.

With formaldehyde and paraformaldehyde as a sizing agent in one-step surface sizing treatments of paper and textiles.

In special coating such as washable board coatings.

For boiler feed water treatment to prevent formation of boiler scale.

For special types of adhesives.

As a waterproof coating in linoleum backing paints.

As a grease-resisting reagent in priming paints which serve as undercoats in linoleum manufacture.

In the form of its sodium salt, alpha protein is used extensively in textile sizing.

In leather finishes where high gloss and tough films are desirable.

Use in the preparation of artificial fiber.

#### GAMMA PROTEIN

Alpha protein is a protein chemically extracted from soybean meal and will analyze 96 per cent protein or above. Gamma protein, on

\* Developed by the Glidden Company.

the other hand, is a protein derived from soybean meal by mechanical means whereby the protein content is brought up to between 53-54 per cent protein. The concentration is brought about through the elimination to a large extent of the hulls and fibrous matter occurring in the soybean meal by very fine milling, screening, etc. A typical analysis of gamma protein is:

Moisture .....	6.07
Protein .....	54.0
300 Mesh .....	1.47
Fat .....	0.70
Fiber .....	2.19

In the manufacture of gamma protein special equipment is necessary to insure very fine texture, 97.5-98 per cent passing through 300 mesh.

Another characteristic of gamma protein is the viscosity when cut with 5 per cent caustic solution. It is quite necessary to have a certain viscosity, particularly when it is used in coatings. The viscosity of gamma protein is subject to a number of conditions. Gamma protein tends to become lower in viscosity on aging, the aging being undoubtedly a denaturing and lowering of solubility.

Gamma protein is finding rather wide application in the coating industry in conjunction with casein. Very successful coating work can be done with mixtures as high as 50 per cent gamma protein and 50 per cent casein. When one considers the high cost of casein and the relatively low cost of gamma protein, the saving to the coating industry in the use of such a mixture is very appreciable.

Gamma protein also is now being formulated in a very satisfactory paste paint. The following is a typical formulation:

1. Gamma protein .....	100 lb.
Karaya O .....	1.5 lb.
2. Water .....	550 lb.
3. Lithopone .....	400 lb.
Asbestine pulp .....	100 lb.
Mineralite 3X .....	100 lb.
4. Sodium hydroxide .....	2 lb.
Water .....	50 lb.
5. Raw Linseed oil containing 0.02% cobalt ...	50 lb.
6. Pine oil .....	5 lb.
7. Dowicide "A" or phenol .....	6 lb.
8. Lithopone .....	400 lb.

Mix No. 1 dry and soak with No. 2 for 15 minutes. Add 3 and agitate at room temperature for 20 minutes. Add 5 and bring temperature to 160-170° and hold for 15 minutes. The mixture should be agitated throughout the entire time.

Add 5 and allow to agitate for 20 minutes at a temperature between 140–160°. Then add 6, 7, and 8 in order. In case Diglycol laurate is available, 5 lb. should be added at the end of step 4.

Considerable variations in this formula are possible depending on the characteristics desired.

Gamma protein has other applications in the industry, and as a result of the high price of casein gamma protein has become quite well established in the paper coating and the paint industry.

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## CHAPTER 17

### ALKYD EMULSION PAINTS

HAROLD C. CHEETHAM and WILLIAM T. PEARCE

Emulsions of a special alkyd resin were introduced in Europe a number of years ago. Since then they have come into successful commercial use both in Europe and America. Applications for patents in United States were made by Frederick Frick in December, 1929, and were later granted.\* Included in these patents is a description of new types of paints which are suspensions of pigments in an aqueous emulsion of an alkyd resin. After drying, the films of such paints are insoluble in water and possess the characteristics of the alkyd resin employed.

#### Emulsions

Emulsions are heterogeneous, dynamic systems. As such they differ in physical characteristics from oil or varnish vehicles and from the common casein aqueous glue bases. Broadly speaking, they may be divided into two components: the dispersed phase and the continuous phase. In the emulsified alkyds, these terms are synonymous with the resin phase and the aqueous phase, respectively. The interfacial film differs from either component in actual composition, but usually differs from the continuous phase only in percentage composition, and may be considered as part of the continuous phase.

**The Resin Phase.** The nature of the alkyd resin may vary within rather wide limits without affecting appreciably the superficial characteristics of the emulsion. Thus, color, viscosity, and hardness may vary over a considerable range in the resin without producing noticeable change in the emulsion. In the dried film, of course, such variations become readily apparent. One characteristic of the alkyd which does have a decided effect upon the properties of the emulsion is its solubility, or the capacity for forming water-soluble salts with dilute bases. Long-oil alkyds show the least reactivity; short-oil alkyds

\* U. S. Patents 2,178,474 and 2,178,475.

show marked salt-forming tendencies, and therefore present difficulties in preparing stable emulsions. Obviously, a resin which is water-soluble or one that reacts readily with ingredients in the aqueous phase to produce water-soluble soaps cannot be emulsified successfully.

Well-dispersed alkyd resin emulsions are milk-white in color, owing to the scattering of light by the dispersed particles, regardless of whether the alkyd itself is relatively good or poor in color. Discoloration in the emulsion develops as the particles increase in size through agglomeration, or when films of dehydrated emulsion form on the surface or on container walls. Partially dried, opaque films of the resin at the surface of the emulsion are likely to appear darker to the eye against the white background of emulsion than dried transparent films of the same resin.

The average particle size of the dispersed alkyd is between 0.5–1.0 micron in diameter. In a good alkyd emulsion, all diameters should be below 1.0 micron and at least 25 per cent of the particles should be less than 0.5 micron in diameter. The average particle size and the range of particle size are factors contributing to the viscosity of the emulsion, but are more important in determining the actual stability of the emulsion, i.e., stability to "breaking," settling, or inversion of phase.

Liquid driers are conveniently added to the resin before emulsification and constitute a part of the resin phase.

**The Aqueous Phase.** The ingredients and general properties of the aqueous phase determine, to a large extent, the properties and behavior of the emulsion. The aqueous phase suspends not only the resin particles but subsequently the pigment particles as well, until the film is formed. When the ratio of resin phase to aqueous phase is high, the apparent viscosity of the emulsion is governed mainly by the concentration factor. Since the emulsion structure is thixotropic, viscosity readings determined with orifice viscosimeters or the plunger type "mobilometer" are arbitrary flow-numbers including yield values, and not true viscosity values. As the ratio of resin phase to aqueous phase is reduced by dilution, the apparent viscosity of the emulsion diminishes rapidly until the viscosity of the aqueous phase itself becomes the determining factor. The viscosity of the aqueous phase is quite independent of the resin phase, excepting in so far as it may be influenced by water-soluble soaps or salts derived from the resin. The viscosity of the aqueous phase is determined by the nature and concentration of emulsifying agents, stabilizers, and wetting agents present.



The viscosity or flow characteristics of the aqueous phase are influenced not only by the specific nature and concentration of the water-soluble ingredients mentioned above but also by the *pH* of the solution, salts present, and changes in molecular size in some of the ingredients. Thus, the viscosity contributed by casein at a given temperature depends upon the kind and quality of casein, the concentration and nature of the peptizing agent, the presence of salts, and the age of the solution. In the presence of water, and particularly when bases are used, the casein molecule gradually degrades to smaller fragments, changing the acid-base relationship and causing a marked decline in viscosity. More stable compounds, such as the cellulose ethers and the alginates, show much less change on aging, but the viscosity of their solutions is also influenced somewhat by changes in *pH*, and to some extent they hydrolyze gradually or break down into smaller molecular fragments.

**Maintenance of *pH*.** In order to obtain the most stable and finely dispersed emulsions, it has been found desirable to emulsify alkyds in slightly basic solutions. For the sake of ultimate water resistance in the resin film, a volatile base which will leave the film on drying and not remain as a water-solubilizing ingredient is the least objectionable. For this reason, ammonia or morpholine is used. Several troublesome features are intimately connected with the necessity of using a volatile base. First, because of its volatility there is some loss in processing, grinding, or mixing with pigments, and during storage. Second, its odor is objectionable to some. Third, it reacts slowly with the emulsifying agents and with the emulsified alkyd to form salts. In such ways, the concentration of base in the emulsion gradually declines. As a result, a decline in viscosity may be noticeable, but the stability and practical usefulness of the emulsion are undisturbed.

**Effect of Temperature Changes.** Emulsions are known to be rather sensitive to temperature changes. Freezing is harmful if carried far enough to cause rupture of the interfacial films and coalescence of resin particles. Freezing of only a part of the aqueous phase, however, causes no appreciable damage to a good emulsion. Therefore, the answer to the question as to whether a frozen emulsion is still usable depends upon the time and extent of the freezing and may be answered in a practical way by microscopic examination of the thawed emulsion. If the dispersion is still good, the emulsion has not been harmed.

Elevated temperatures are distinctly harmful to emulsions and usually cause rapid "breaking" or coalescence of dispersed particles.

Everyone knows that certain irreversible changes take place in heated milk, a typical natural emulsion. Alkyd emulsions are more stable than milk, yet they too are sensitive to elevated temperatures. All the possible reactions of ammonia with other ingredients present are tremendously accelerated by heat. Likewise, the viscosity of the aqueous phase suffers reduction, the strength of the interfacial film declines, and the velocity of movement of the dispersed resin particles increases, so that the tendency for coalescence is greatly increased.

The effects of elevated temperatures are sometimes difficult to analyze. If the temperature has not been severe enough to cause increase in particle size in the dispersed phase, the only marked change may be a drop in viscosity as a result of degradation of the emulsifying agent, dissipation of ammonia, and an increase in soluble ammonium salts. If the actual stability of the emulsion has been disturbed, a marked thickening or gelation may occur. The two effects work in opposite directions and may mask each other. Here, again, a microscopic examination is helpful.

**Emulsifying Agents.** To facilitate the mechanical operation of emulsification and to stabilize the emulsion against mechanical and thermal shock, i.e., to prevent the two phases from separating into layers or agglomerates, certain emulsifying agents in relatively low concentration are used. Their presence is undoubtedly deleterious to the ultimate alkyd film, affecting particularly water resistance, color, durability, permeability, etc., unless their concentration is low enough so that they are dissolved in the resin phase as the film forms. Casein is one of the most effective agents, but, unless it is used in a suitable form, it can be a source of many difficulties.

**Film Formation.** When the emulsion is spread upon a surface in a thin film, water evaporates, the emulsion breaks, and the resin particles coalesce to form a continuous, homogeneous, clear film. At first the film must remain relatively permeable to moisture so that water may escape, which is the first stage in drying. The second stage, that of drying by oxidation of the alkyd resin, then takes place. This latter drying stage is probably retarded and somewhat slow in comparison to that of common alkyd resins in organic solvents, owing to the retarding effect and retention of water in the resin film. The ultimate film of resin contains all the residues of ingredients present in the aqueous phase. Most of these ingredients are somewhat hydrophylic in nature, and, therefore, the water sensitivity and ultimate durability of the film are dependent upon their concentration and con-

dition in the film. Satisfactory adhesion and other film properties are best when there is no evidence of separation, spewing, sweating, or oiliness in the dried resin film.

**Inversion of Phase.** When the volume of resin phase exceeds 70 per cent of that of the entire emulsion, the emulsion becomes susceptible to inversion, i.e., the aqueous phase becomes dispersed in the resin. The emulsion is then no longer readily dilutable with water and has a sticky feel. By slow agitation and gradual addition of water, an inversion back to the desired phase relationship may be accomplished.

### **Manufacture of Paints**

Emulsified alkyds have been successfully developed and used commercially in the production of paints which have outstanding properties. The discussion which follows refers to this use of special emulsified alkyds which were developed for this purpose. It does not necessarily follow that any alkyd emulsion would give the properties described or be satisfactory for the uses mentioned.

It is not possible to make broad statements regarding the use of alkyd emulsions in general. The emulsion is a very complex system, especially a pigmented emulsion, and there is room for wide variations in behavior. Such properties as brushability, rate of drying, waterproofness, and durability vary widely with emulsions of alkyd resins. A very careful control of all factors involved is necessary if satisfactory results are to be obtained.

Alkyd emulsions available usually contain 40 to 50 per cent solids. Drying oil-modified alkyd resins which possess good durability and color retention should be used. The dry film is similar to the film which would be secured by using the alkyd resin in organic solvents which, in addition to durability, should possess hardness, water resistance, and satisfactory adhesion. Emulsified alkyds give films of satisfactory durability, and may be used in formulating either interior or exterior paints. Owing to the absence of the solvents normally employed in paints and varnishes, they are free from the objectionable "paint" odors. Compared with oil paints, this type of finish is easier to apply and gives cleaner shades. It may be applied to wet surfaces. The presence of a small amount of moisture in the surface painted is much less likely to cause blistering and peeling.

Properly made emulsions possess good wetting properties and may be used with a great variety of pigments, water-dispersible pigments being preferred. Such pigments as zinc oxide, white lead, iron blues,

whiting, and asbestine cannot be employed, but titanium dioxide, barium titanium pigment, lithopone, china clay, silica, and mica are quite satisfactory. Because such paints are usually applied to plaster, the pigments which are resistant to lime and cement should be used.

**Manufacturing Procedure.** The aqueous emulsion and the pigments are mixed in the usual way. The paste is then passed through a stone or roller mill. In many cases only one mixing is necessary. The mills should be loosely set so that the stones or rolls do not become hot in order not to affect the dispersion of the resin. It is more satisfactory to supply these paints in the form of heavy pastes, employing only enough water to insure good handling. Such pastes are readily reduced with water before application. During the manufacture of the emulsion, preservatives are added in sufficient quantity to prevent the growth of molds and to prevent putrefaction in the emulsion at the concentration in which it is supplied and also in concentrations in which it will be present in paints of several types. For the prevention of putrefaction such preservatives as phenol and cresylic acid are used. Borax is added to prevent the growth of molds. The employment of very high ratios of pigments requires the use of additional quantities of preservatives. Paints reduced for painting should also have additional quantities of preservatives if they are not used in reasonable lengths of time.

The correct reduction to secure proper application must be determined for each formulation.

The ratio of binder to pigment depends, as in other types of paints, upon the purposes for which the paint will be employed. Durable exterior white paints should contain approximately one part by weight of binder to one part of pigment. A good interior paint would contain five or six parts by weight of pigment to one part of binder.

A typical formulation of an exterior and an interior paint is given below.

#### EXTERIOR WHITE

Titanium dioxide (water-dispersible) .....	100 lb.
Barium titanium pigment (extra strength) .....	100 lb.
Flake mica (not ground) .....	25 lb.
Silica .....	25 lb.
Alkyd emulsion (50% solids) .....	400 lb.

For application reduce each gallon of paste with 1 to 1¼ gallons of water for the first coat and with 3 quarts of water for the second coat.

## ALKYD EMULSION PAINTS

## INTERIOR WHITE

Titanium dioxide (water-dispersible) .....	200 lb.
Barium titanium pigment .....	200 lb.
Colloidal silica .....	150 lb.
Flake mica .....	50 lb.
Alkyd emulsion (50% solids) .....	200 lb.
Water .....	450 lb.

For application reduce each gallon of paste with one quart of water.

**Uses.** Alkyd emulsion paints dry quite rapidly, and in good drying weather two coats may be applied the same day. The speed of drying, freedom from paint odors, and the washability make them especially suitable for use in apartment houses, hotel rooms, and offices. Paints may be applied during the day and rooms occupied in the evening, or applied at night and used the next day. This type of finish is especially suited for porous surfaces of all kinds including concrete, stucco, plaster, brick, and fiberboard. By varying the ratio of pigment to non-volatile binder, paints suitable for a wide variety of uses may be formulated. In the case of wood and metal, an oil type primer should be employed.

This type of paint has also been successfully used over asphalt coatings and as a sealer coat over fresh plaster.

# LACQUERS



## CHAPTER 18

### LACQUER—NITROCELLULOSE

ALBERT O. PLAMBECK and JULIUS F. RUDD

#### DEFINITION

The word "lacquer" is generally considered to indicate a liquid coating, made up of volatile and non-volatile portions, which dries rapidly and leaves a hard tough film when applied in thin coats. Webster's *Dictionary* mentions four types of lacquer:

(a) A spirit varnish, as shellac, often colored, used especially for coating brass and other metals to heighten their lustre or prevent tarnishing.

(b) Japanese or Chinese Lacquer, the chief constituent of which is urushiol, obtained by tapping the Japanese varnish tree, straining and drying the sap by heat. To the resulting dark brown syrupy liquid are usually added diluents, pigments, etc. Burmese lacquer and Formosan lacquer contain thitsol or laccol in place of urushiol. Lacquer forms a remarkably tough and durable coat, and is applied to wood, porcelain, metal or the like. In fine lacquer work as many as 20 or 30 coats are applied, each coat being ground smooth.

(c) Any of the various artificial varnishes or varnish paints, usually colored and often opaque, in which pyroxylin, resins (natural and synthetic), ester gum, asphalt, cellulose acetate, etc., serve

(d) An oleoresinous coating for food containers, usually hardened by baking.

Although the products first named were formerly known as lacquers, the present-day *lacquer* refers primarily to nitrocellulose (pyroxylin) coatings, which may be either clear or pigmented.

Nitrocellulose lacquers have an advantage over the oleoresinous coatings for the following reasons:

1. They dry by evaporation, a fast process as compared with the relatively slow process of oxidation which causes the air drying of oleoresinous finishes.



2. Owing to the chemical control of raw materials, such as nitrocellulose, solvents, resins, and plasticizers, more uniform production results are obtained.

3. Owing to speed of application, drying and ease of handling, there is less necessity for expensive production equipment, small floor space is required, and there are fewer rejects.

4. They have remarkable durability, water resistance, mar and abrasion resistance, hardness, color retention, chemical resistance, flexibility, and toughness, all of which properties place nitrocellulose lacquers among the highest-quality protective coatings.

5. The manufacture and control of nitrocellulose lacquers is more of a chemical and technical problem than the making of varnishes and paints because of the chemical nature of the ingredients used, chief of which is nitrocellulose.

### HISTORY

Nitrocellulose, or "pyroxylin" lacquers first came into commercial use in 1855 in England, when Alexander Parkes (7) was granted a patent covering the use of a liquid nitrate composition as a protective coating. Early progress was slow, owing to the nature of the limited number of solvents then known as well as the limited knowledge of nitrocellulose itself. Ether and alcohol solvent mixtures of nitrocellulose became fairly well known but were only slightly used as protective coatings. The extreme rapidity of evaporation of these solvents caused condensation of moisture on the surface of the coating, with subsequent precipitation of the nitro cotton. The film produced was weak, milky white in appearance, and lacked adhesion and proper tensile strength. This phenomenon, known as blushing or "blooming," made the early lacquers unsuitable for general industrial use. They were satisfactory, however, for "new skin" for covering cuts and abrasions of the skin as well as other medical preparations. Development of ester type solvents, such as ethyl, butyl, and amyl acetates, along with discovery of low-viscosity cotton, resulted in phenomenal increase in commercial and industrial use of nitrocellulose lacquers. Never in the history of the paint and varnish industry had any product increased so rapidly in industrial demand. Exact growth in volume is shown in the table on page 499, which also gives the value of lacquer production. An interesting feature of this table is the large increase in gallonage, together with a steady decrease in average value per gallon, with the exception of the year 1929.

## LACQUER PRODUCTION STATISTICS

(From Bureau of the Census, U. S. Dept. Commerce (10) )

<i>Year</i>	<i>Total Gallons</i>	<i>Value</i>	<i>Average Value \$ per Gallon</i>
1925	12,265,206	\$27,254,796	\$2.22
1927	30,836,168	64,522,406	2.09
1929	32,959,856	82,336,227	2.50
1931	29,403,418	47,181,151	1.60
1935	42,278,656	55,097,453	1.30
1937	56,847,454	72,272,824	1.27
1939 *	51,823,489	64,316,521	1.24
1940 *	47,969,129	61,273,829	1.26
1941 *	64,504,681	84,070,734	1.30
1942 *	49,441,510	70,924,502	1.44

\* Representing approximately 84% of total.

Physical characteristics of high viscosity and too rapid drying at first limited application to spraying or dipping. Improvements in solvents through developments in synthetic chemistry made possible the production of materials suitable for brush application. Brushing lacquers made heavy inroads on the sale of oleoresinous finishes for household utility and decoration and stimulated development of four-hour and other fast-drying oleoresinous varnishes and enamels which were the answer of varnish and enamel manufacturers to the brushing lacquer competition. Lacquer competition was no doubt the chief stimulus in development of the newer types of synthetic resin finishes, such as phenol-formaldehyde-oleoresinous combinations, also air-dry and baking alkyd, and urea resin type materials.

Other cellulose derivatives, such as ethylcellulose, benzylcellulose, cellulose acetobutyrate, and cellulose acetate, are also used commercially, but nitrocellulose is, by far, the largest in volume.

## MANUFACTURE OF NITROCELLULOSE

The nitrocellulose is made from cotton linters, which are the short fibers remaining on the cotton seed after the long fibers have been removed by the cotton gin for textile purposes. Impurities, such as oils and non-cellulosic materials, are removed by boiling in caustic solution, and thus the pure white fibers are obtained. This mass is washed and then treated with nitric and sulfuric acid mixtures until the proper degree of nitration is reached. This nitration is carefully controlled. The nitrocellulose is washed first with water and then the

water is displaced with ethyl alcohol. In this form, wetted with 35 per cent alcohol, the product is safe for shipment and for use in the lacquer industry. Recently, some nitrocellulose has become available which is made from a wood pulp base, but this product has not been considered as high in tensile strength and durability as that made from cotton linters.

Nitrocellulose is the basic film-forming ingredient of pyroxylin lacquers, as it forms a thin, hard, tough, clear film which is nearly colorless. It functions in lacquer as drying oils do in varnish, but forms a harder, tougher film. The drying time is governed by the solvents used. Nitrocellulose and solvents alone produce a film which is too hard and tough, and slightly brittle. Since the strength of cohesion is greater than the adhesion of the film, a simple nitrocellulose film is easily pulled loose from the surface on which it was applied. It comes off in strips or sheets. It was therefore found necessary to incorporate resins in lacquer (nitrocellulose plus solvents) to develop greater adhesion to the surface. Resins also add luster, increase depth or body of the film, and decrease the cost of the finished lacquer, as most resins are lower in cost than the nitrocellulose. Then further to develop elasticity in a lacquer, other ingredients are used; they are chemical plasticizers, and/or drying and non-drying vegetable oils. Beside the nitrocellulose, resin, and plasticizers, solvents for the nitrocellulose, such as acetates or ketones; latent solvents, such as alcohols, and resin solvents, diluents, are also required to make a finished lacquer. The resin solvents are commonly known as diluents; being low in cost, they are a factor in reducing the final cost of the lacquer.

### Types of Nitrocellulose

Several types of nitrocellulose are commercially available. Among them are:

1. Regular soluble (R. S.) nitrocellulose has a nitrogen content of 11.80 to 12.20 per cent by weight. R. S. nitrocellulose is supplied in viscosities of  $\frac{1}{10}$  second,  $\frac{1}{4}$  second,  $\frac{1}{2}$  second, 5-6 seconds, 8-10 seconds, 15-20 seconds, 30-40 seconds, 60-80 seconds, 125-175 seconds, 250-400 seconds, and 900-1,300 seconds. The R. S. nitrocellulose is soluble in the ester solvents, ketones, and in alcohols with esters or ketones.

One-tenth second, or 18-25 centipoises, is an exceedingly low-viscosity grade. The film obtained with this material is less flexible but is equally as hard as that obtained with higher viscosity types. It is used in lacquers where an unusually high solid content is desired.

When used in conjunction with some of the softer types of resins, which require a large amount of nitrocellulose, special types of lacquers are obtained which produce a good finish in one coat.

The  $\frac{1}{2}$  second type is most widely used in automobile, furniture, and other lacquers of good durability. The 5–7 second viscosity nitrocellulose is used extensively in all types of industrial lacquers. The higher viscosity types, 8–10 seconds and higher, are used in lacquers, coated fabrics, artificial leather, window shades, airplane dopes, leather cement, photographic film, and various other special applications.

2. Alcohol-soluble (A. S.) nitrocellulose has a nitrogen content of 11.40 to 11.70 per cent by weight. It is made in viscosities of  $\frac{1}{2}$  second, 30–40 seconds, and 300–500 seconds. This type will stand a higher dilution with alcohol before precipitation as compared with the R. S. type, which will take a higher toluol dilution. This is of importance in certain formulations where alcohol-soluble resins are used, or where the use of coal tar diluents is inadvisable.

3. Spirit-soluble (S. S.) nitrocellulose is made with a nitrogen content of 10.80 to 11.10 per cent. This type of nitrocellulose is available in several viscosities, as  $\frac{1}{4}$  second and 5–6 seconds. It is completely soluble in the SD No. 1 grade of alcohol. The addition of a small quantity of toluol or other hydrocarbon improves the clarity of the solution, and a small amount of ethyl acetate speeds up the rate of solution. It finds usage in odorless lacquers, wood sealers, and certain lacquers containing alcohol-soluble resins, such as shellac, and Manila resin.

4. Bronzing nitrocellulose has a nitrogen content of 11.80 to 12.4 per cent by weight and is supplied in viscosities of 35 to 40 seconds, and 60 to 80 seconds. This type is specially prepared to hold bronze powders in solution with the minimum gelling tendency. The esters and ketones are employed as solvents in bronzing lacquers.

5. Silver lacquer nitrocellulose is made in viscosities of 20–30 seconds and 60–80 seconds. This type of nitrocellulose gives a clear water-white solution without any haze, and is used where palest color is required. It is widely used in the manufacture of clear silver lacquers such as are applied on silver articles and other highly polished surfaces where a thin film is desired to prevent tarnishing.

## Viscosity

Since viscosity plays an important part in nitrocellulose technology, let us consider some of the available data on this subject. The following data are taken from the *Nitrocellulose Handbook*, published

by the Hercules Powder Company, and are representative of the general views on viscosity in connection with nitrocellulose lacquers (3).

Viscosity is the property of a fluid by which it resists continuous deformation, especially characteristic of thick liquids. Viscosity is the reciprocal of fluidity.

When nitrocellulose is treated with various organic liquids or mixtures of liquids it is dispersed, forming clear colloidal solutions. These solutions are of industrial value. One of the valuable properties of nitrocellulose is that various types of nitrocellulose give solutions differing widely in viscosity although the same concentration of nitrocellulose, or conversely, requires widely different amounts of solvent to produce solutions having the same viscosity. The main need of having the various viscosity types is the desire to obtain nitrocellulose films of varying thickness.

*Importance of Viscosity.* The importance of viscosity in the use of nitrocellulose makes it necessary to measure accurately this property, so that in using various solutions made from time to time they will work alike. The viscosity of the solution obtained depends not only on the nitrocellulose used, but also on a great many other factors. However, the nitrocellulose is a very important factor, which makes it necessary to measure this property accurately to assure the user that when he uses similar lots received from time to time he will obtain the same results. In addition, the same property of nitrocellulose that gives solutions having varying viscosities also is a factor in the strength of the product in which the nitrocellulose is used. Therefore, it is very important that this property be uniform in different lots used from day to day.

The viscosity is measured by the shearing stress in dynes per square centimeter required to move either of two parallel planes, one centimeter apart relative to each other, with a velocity of one centimeter per second, the space between the planes being filled with that fluid. It is measured in poises or preferably in centipoises, the centipoise being the approximate viscosity of water at 20° C. (1.005 cps.).

*Measurement Methods.* There are different types of instruments to measure the viscosity of liquids, such as those based on the time for a ball to fall through the solution, for air bubbles to rise through a capillary, for the solution to flow through an orifice, work necessary to rotate discs and cylinders in the solution.

The Hercules Powder Company has adopted the falling ball method, as the most suitable method for the purpose. The falling ball viscometer was developed from Stokes' mathematical derivation of the relation between the viscosity of a liquid and the rate of fall of a small sphere through the liquid. In this derivation the assumption was made that the ball fell through liquid of infinite extent. The resulting formula calls for correction factors as one is unable to employ an infinite sea of liquid in a practical test; however, Ladenburg developed the equation for these corrections.

This Company has carefully determined the correction factors for the specified apparatus and the tolerance necessary to maintain an accuracy of  $\pm 3.8\%$  (exclusive of stop watch errors) with the instrument standardized.

*Instrument Specifications.* The method consists in noting the length of time required for a ball to fall a definite distance through the liquid being tested (which is contained in a glass tube of definite uniform diameter), the whole being

maintained at a definite temperature. The parts used in the instrument adopted by the Hercules Powder Company have the following specifications:

The glass tube is 355 mm. (14 in.) long, having a uniform internal diameter throughout its entire length of  $25.0 \pm 0.5$  mm. ( $0.984 \pm 0.02$  in.). This specification should be followed very closely, as small variations in tube diameters cause large errors in results. Even the small tolerance of  $\pm 0.5$  mm. allows a variation in results of  $\pm 2.2\%$ . Two marks  $254.0 \pm 0.8$  mm. ( $10.0 \pm \frac{1}{32}$  in.) apart are to be etched on the tube, so that each mark is approximately 50 mm. (2 in.) from an end of the tube. One end of the tube is to be closed by means of a cork stopper wrapped in tinfoil.

The balls are to be well made of steel, with a diameter of  $7.938 \pm 0.01$  mm. ( $0.3125 \pm 0.0005$  in.) and weighing  $2.0385 \pm 0.0007$  gram. A large percentage of  $\frac{5}{16}$ -inch steel ball bearings on the market will pass these specifications.

The time is to be noted by the use of a good stop watch reading  $\frac{1}{5}$  of a second.

The temperature is to be noted from a thermometer which can be read to  $0.1^\circ$  C.

*Temperature Requirements.* The apparatus used to maintain the proper temperature will depend on the number of tests to be made and the accuracy desired. If a large number of tests of high accuracy are to be made, a constant temperature water bath should be provided capable of maintaining a temperature of  $25.0 \pm 0.1^\circ$  C. If less accurate results are satisfactory a less constant water bath can be used. If only a few tests are to be made, the temperature should be accurately noted and the reading obtained should be corrected by the use of suitable factors.

The time in seconds multiplied by 377 gives the viscosity in centipoises at the temperature specified, of the standard test solutions. This factor will differ for any instrument not within the above specifications.

The following procedure has been standardized by the Hercules Powder Company for determining the viscosity of nitrocellulose of various types.

*Solution Formula:*

Nitrocellulose (dry) .....	12.2% by wt.
No. 1 denatured ethyl alcohol .....	22.0%
Ethyl acetate .....	17.5%
Toluol .....	48.3%

Two hundred grams of the above solution are required, the ingredients to be weighed with an accuracy of  $\pm 0.02$  gram. The solutions can be made most conveniently by using eight-ounce, wide-mouthed bottles fitted with cork stoppers wrapped in tinfoil. The solution of the nitrocellulose will be hastened if the alcohol and toluol are added first and allowed to wet the nitrocellulose thoroughly before adding the ethyl acetate. The solution can be expedited by slowly shaking the bottles in any form of mechanical shaker.

The nitrocellulose must be dried thoroughly; otherwise an incorrect weight of nitrocellulose will be used in the test solution. The errors caused by incorrect drying and weighing can be calculated from the concentration-viscosity curves (Figs. 1 and 2).

*Drying Nitrocellulose.* If a fairly large amount of nitrocellulose is to be dried for viscosity tests or for laboratory tests on formulating lacquers, hot air blowers should be used. These blowers are designed to blow compressed air under 60 pounds pressure heated to  $65^\circ$  to  $75^\circ$  C. through the nitrocellulose. In designing



If compressed air and steam are not available, and if only small quantities are dried occasionally, a suitable method would be to dry it in a water-jacketed oven equipped with a water gauge and heated by an electric hot plate. In drying the

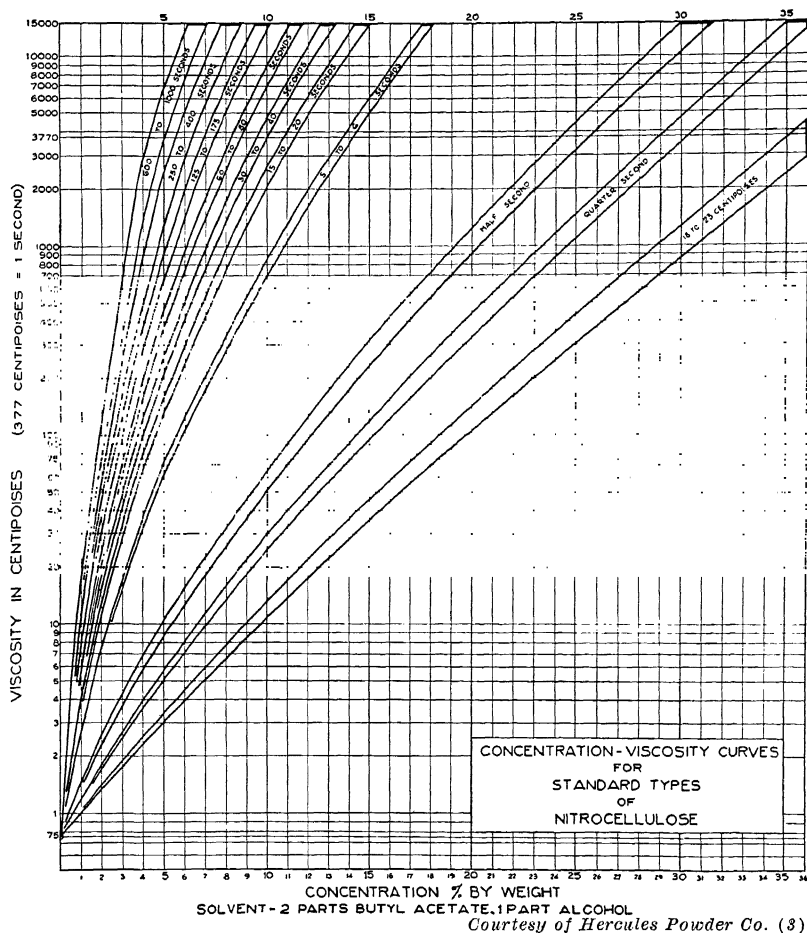


FIG. 2.

nitrocellulose in these ovens it should be spread in paper trays in layers not over one inch deep. If this method is used, care should be taken to have the latch removed from the door of the oven, and to let no nitrocellulose dust accumulate inside the oven or get on the hot plate. Nitrocellulose wet with denatured ethyl alcohol should be dried eight hours at 80° C.

*Suction Drier.* Another simple method for drying nitrocellulose, which uses apparatus found around every laboratory and at the same time does not present



the hazards from dry nitrocellulose dust that drying in ovens does, is to use a water aspirator pump to draw air heated in the usual laboratory electric oven through the wet nitrocellulose. The brass pipe should be about  $1\frac{1}{2}$  inches in diameter and 12 inches long, as these proportions give about the most efficient results. The pipe should be lagged with asbestos to prevent heat losses. A thistle tube, or funnel, the mouth of which is covered with a silk cloth, is inserted in one end to act as a screen. An indentation may be made in the sides of the funnel to allow a thermometer to pass through. The funnel, as well as the thermometer, is held in place by means of a stopper which also seals the end of the brass pipe. The tube is connected to a water aspirator pump, such as the Boekal Type given in Eimer & Amend Catalog, No. 30,134 large size, through a suction flask or other container to act as a trap for any water that may back from the pump. The other end of the brass tube is to be connected to one of the top vents of an electric oven such as a Freas, Thelco, or similar type fitted with a thermo regulator. Using an oven temperature of  $85^{\circ}\text{C}$ . and 35 lb. water pressure on the pump specified, satisfactory drying is obtained in four hours using nitrocellulose wet with ethyl alcohol.

On setting up any apparatus for drying nitrocellulose, particular attention should be paid to taking proper care of dry nitrocellulose dust as it is exceedingly inflammable. After setting it up, the first thing to determine is the proper length of time required to dry the nitrocellulose completely. The time required will vary with diversified drying conditions.

*Solvent Specifications.* The ethyl acetate used should have an ester value of 85–88%, a specific gravity of 0.887 to 0.893 at  $15.5^{\circ}/15.5^{\circ}\text{C}$ ., and 90% distill between  $70\text{--}80^{\circ}\text{C}$ . with a dry point of  $90^{\circ}\text{C}$ .

The No. 1 CD ethyl alcohol used should be pure alcohol containing not less than 92.3% weight of ethyl alcohol and denatured according to the approved government formula.

The toluol used should have a specific gravity of 0.864 to 0.874 at  $15.5^{\circ}\text{C}/15.5^{\circ}\text{C}$ ., at  $2^{\circ}\text{C}$ . boiling range including boiling point of toluene ( $110.4^{\circ}\text{C}$ .), and be non-corrosive.

The solutions prepared as described above are allowed to stand for 24 hours after they have been mixed, in view of the fact that the viscosity of nitrocellulose solutions continues to change for some time because of continued dispersion of the nitrocellulose even after the nitrocellulose appears to be completely in solution. During this 24-hour period, the solution should not be subject to widely fluctuating temperatures and should be kept preferably at  $25^{\circ}\text{C}$ . in the constant temperature bath.

*Constant Temperature Bath.* In making the test, the 25 mm. tube is filled with the nitrocellulose solution and is set in a vertical position in the constant temperature bath at  $25^{\circ} \pm 0.1^{\circ}\text{C}$ . If the temperature of the solution is several degrees different from the temperature of the water bath, it will take at least one hour for the solution to reach the proper temperature. After the solution has reached the proper temperature the steel ball is dropped from the surface of the solution down the center of the tube. With the stop watch, the time is noted in seconds that it takes the steel ball to fall from the upper etched mark to the lower mark.

If not enough tests are made to warrant a constant temperature bath, the temperature should be accurately determined and the viscosity as measured should be corrected by the following formula:

$$\log V = \log V_1 + 0.0207(T_1 - T)$$

(Where  $V$  is the viscosity in seconds corrected to temperature  $T$ , and  $V_1$  is the viscosity in seconds observed at temperature  $T_1$ , the temperature being expressed in degrees centigrade.)

The above equation will give the effect of temperature on viscosity of nitrocellulose solutions containing varying concentrations of nitrocellulose, nitrocellu-

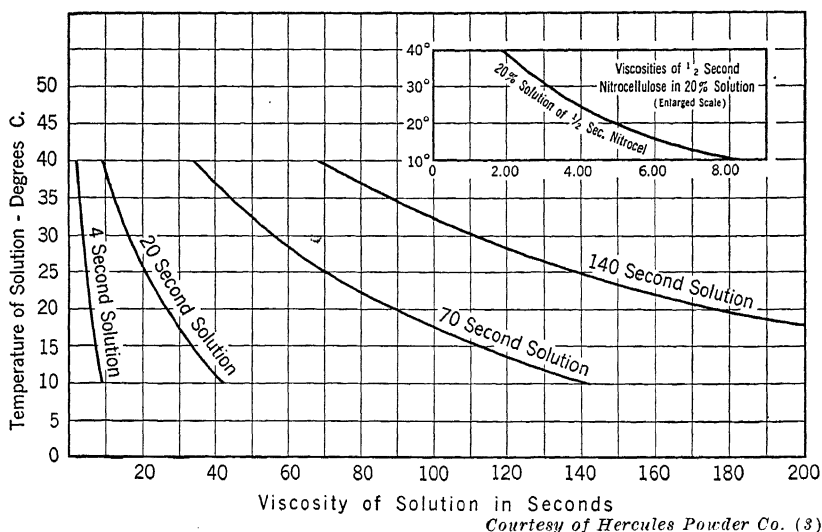


Fig. 3. One-half Second to 140 Seconds Viscosity Curves Showing Temperature and Viscosity Relation.

lose of any viscosity, and possibly all the commonly used mixtures of solvents.

The effect of temperature on the viscosity of nitrocellulose solutions is not often appreciated. Figure 3 indicates graphically the effect of temperature on the viscosity of solutions used in testing nitrocellulose.

*Method for Half-Second Nitrocellulose.* When half-second nitrocellulose is used in the above formula, the solution has a viscosity of approximately 120 centipoises. Such a solution in the above apparatus has a theoretical time of fall of less than 0.5 second. In view of the fact that such a rate of fall does not measure viscosity, the following formula is used in place of the standard formula:

Half-second nitrocellulose .....	20% by wt.
No. 1 CD denatured ethyl alcohol ....	20%
Ethyl acetate .....	16%
Toluol .....	44%

In all other respects the method is exactly the same as the standard.

*Method for Quarter-Second Nitrocellulose.* Quarter-second nitrocellulose, when used in the standard formula, has a viscosity of approximately 50 centipoises or a theoretical time of fall of less than 0.25 second in the standard apparatus. Consequently the following formula is used for testing quarter-second nitrocellulose:

Quarter-second nitrocellulose .....	25.0% by wt.
No. 1 CD ethyl alcohol .....	18.7%
Ethyl acetate .....	15.0%
Toluol .....	41.3%

In all other respects the method is exactly the same as the standard.

Since the falling ball method of viscosity determination is applicable only to clear solutions, other methods and apparatus find wide usage for viscosity measurement of colored and pigmented lacquers. Of these, the Ford cup and other similar devices have been found suitable for production control of medium-viscosity lacquers. These depend upon measurement of the time required for a given amount of the lacquer to flow through a standard-sized orifice. The Gardner Mobilometer, MacMichael Viscosimeter, and others have been found more advantageous for materials of higher viscosity.

### Viscosity Patents

In 1927 E. I. Du Pont de Nemours & Company, Wilmington, Delaware, obtained a reissue on their patents \* on the use of low-viscosity nitrocellulose in lacquers. Low-viscosity nitrocellulose was classified as all nitrocellulose having a viscosity reading up to 4.6 seconds as measured by the falling ball method. This also covered any blends of high-viscosity and low-viscosity nitrocellulose which had a resultant reading of 4.6 seconds or below. Furthermore, the use of known methods of reducing the viscosity of high-viscosity lacquers was prohibited.

After some lengthy court battles, the patent rights were upheld, and the lacquer industry faced a rather dark future. However, the du Pont Company issued licenses for the use of low-viscosity nitrocellulose, thus enabling the qualified manufacturer to use this important raw material.

### Film Scrap

Motion-picture films are employed to make film scrap, and as produced today are made from nitrocellulose of 11.2 to 11.8 per cent

\* Reissue 16,803, 1,535,438, 1,636,319, 1,710,453, 1,770,108.

nitrogen content, which is the commonly known alcohol-soluble (A. S.) cotton. Two grades of film are commonly used by the motion-picture producers: one for newsreel and short film, which contains 10 to 20 second viscosity cotton, and one for feature and longer pictures, containing 30 to 40 second cotton. The plasticizer content of the original film before exposure is between 19 and 20 per cent, and is essentially camphor. Extensive research has improved the quality of the nitrocellulose used in film stock, but has failed to develop any substitute for camphor as a plasticizer. The principal requirements for motion-picture film are maximum tensile strength, abrasion resistance, and clarity. With the large increase in production of movies, and relatively short life of the sound pictures, large quantities of film are available for film scrap at attractive prices.

The "used" or "junk" films are sorted and graded, and washed free from the photographic gelatin and silver salts, usually by a continuous mechanical scrubbing process in a suitable bath. The wet film is wiped off on revolving drying pads or towels, after which it passes through a drying chamber. It is then rewound on reels. A crystal-clear and water-white stock is thus obtained which serves as a low-priced medium-viscosity nitrocellulose, commercially known as film scrap. The camphor content is reduced to approximately 6 per cent in the washing and drying process, so that the dry film scrap may be considered as containing 94 per cent nitrocellulose and 6 per cent camphor. The camphor content is lessened in a finished lacquer, when other solid ingredients such as resins, oils, pigments, or additional plasticizer are added. The camphor is also advantageous in decreasing the amount of expensive chemical plasticizer which is required in most lacquers for application on wood, metal, or textiles. Comparative tests have shown that the durability and tensile strength of lacquers made from film scrap compare very favorably with lacquers of the same composition made from virgin nitrocellulose. This may be due to a stabilizing effect of camphor on the nitrocellulose, which is not found with other plasticizers.

Motion-picture film scrap is available on the market in dry form, in reels, or small flakes or chips, and in standard solutions containing 24 to 32 ounces of dry film to a gallon of solvent mixture. These solutions are used in large volume in the artificial leather and textile coating industries, and to some extent in non-royalty viscosity lacquers where low cost is essential in order to get volume business.

### SOLVENTS

Solvents perform the function of putting the nitrocellulose lacquer in workable liquid form so that it can be applied or spread on surfaces. The method of application as well as the solid ingredients in the lacquer govern the selection of solvents. A lacquer made for dip application would require a different solvent combination from one intended for brush application. Also, if we consider spraying lacquers alone, some are required to dry slowly and others are required to dry rapidly; each is formulated with different solvents to fit specific production schedules.

Solvents are divided into three main classes: solvents, latent solvents, and diluents. The solvents are mainly the esters, ketones, etc.; these are good solvents for the nitrocellulose. The latent solvents are the alcohols, ethyl, butyl, and amyl; alone, they have no solvent action on nitrocellulose but, admixed with solvent, they become active as solvents for the nitrocellulose.

The diluents are the petroleum thinners of the normal and high solvency type and the coal tar solvents. These are not solvents for nitrocellulose, but are solvents for the resins. They are also used to reduce the cost of the lacquers. The functions of solvents and diluents are discussed in detail in Chapter 27, Volume I.

In general, no one solvent possesses all the requirements necessary to make a satisfactory lacquer; a blend of several solvents is necessary. The ideal solvent should be a good solvent for both the nitrocellulose and the resin or resins in the lacquer. To secure a perfectly clear, homogeneous film and to minimize tendency toward blushing, particularly in the faster-drying lacquers, the solvent should be preferably non-hygroscopic, and not miscible with water. The presence of higher boiling solvents, which evaporate more slowly from the film, will counteract the effect of such fast-evaporating solvents which may of necessity be present in the formulation.

The odor of solvents or diluents is of importance because most lacquers are applied indoors, where the usual method of spray application may throw a large amount of vapor into the atmosphere in a short time. Proper exhaust fans are of great help, but selection of solvents with least objectionable odors is desirable.

Solvents and diluents should be pale or water-white, particularly when used in clear lacquers, white, and delicate tint lacquer enamels. This color requirement is important not only in the original liquid

state but also during storage in drums and metal containers. Any solvent which has a tendency to darken through oxidation or resinification during storage is deleterious to best results. Materials which have such properties are uncommon, and thus easy to avoid.

Toxicity of solvents is another important consideration, particularly when the lacquer user may be exposed to considerable volume of the vapors thrown into the air during evaporation of the solvents. Methanol, or wood alcohol, and benzol are toxic, and should be avoided wherever possible. Toxicity is discussed in detail in Chapter 27, Volume I.

Solvents are conveniently classified for comparative purposes according to their boiling points:

Low boilers:	Boiling point below	100° C.
Medium boilers:	Boiling point between	110 and 145° C.
High boilers:	Boiling point between	145 and 170° C.
Extra high boilers:	Boiling point higher than	170° C.

**Low boilers** serve the function of reducing viscosity of the lacquer so that it can be sprayed. They evaporate quickly, thus giving the lacquer its quick-drying characteristics. They have for the most part rather pleasant odors, and are the least expensive solvents for nitrocellulose. Ethyl acetate, methyl ethyl ketone, acetone, and isopropyl acetate are the most important commercially.

**Medium boilers** impart flow to the lacquer, retard blushing, and are used in large proportion to balance the formula, and to some extent function similarly to the high boilers. Butyl acetate, butyl alcohol, and amyl acetate are most commonly used.

**High boilers** remain in the film longest and act as residual solvents. They impart the final flow to the lacquer and are highly instrumental in giving gloss and smoothness to the finish. They should be strong solvents for both the nitrocellulose and the resins present in the lacquer. Their evaporation should leave a smooth, homogeneous film, which will provide all the qualities of luster, adhesion, and durability which could be expected of a properly designed lacquer. Ethyl lactate, butyl propionate, and diacetone alcohol are the most important.

**Extra high boilers** are those solvents which have extremely high boiling ranges and have very slow evaporation rates. They are used in architectural and brushing lacquer and also specialties. They hold a wet edge which is desirable in coating large surfaces. They are also useful to overcome extreme conditions of humidity and consequent stubborn cases of "blushing." Some of these are butyl Cellosolve, butyl lactate, and octyl acetate.

Although a comparison of the boiling points of solvents gives some indication of their relative rates of evaporation, it has been shown that the two are not always parallel functions. Also, solvent mixtures may evaporate at very different rates from what would be expected from the examination of the boiling points of the component liquids. The charts of comparative evaporation rates and boiling ranges of lacquer solvents compiled by A. K. Doolittle (2), and shown in Figs. 4, 5, 6, 7, 8, and 9, are of inestimable value to the lacquer formulator. Table I gives other chemical and physical properties of lacquer solvents, compiled, also, by A. K. Doolittle (2).

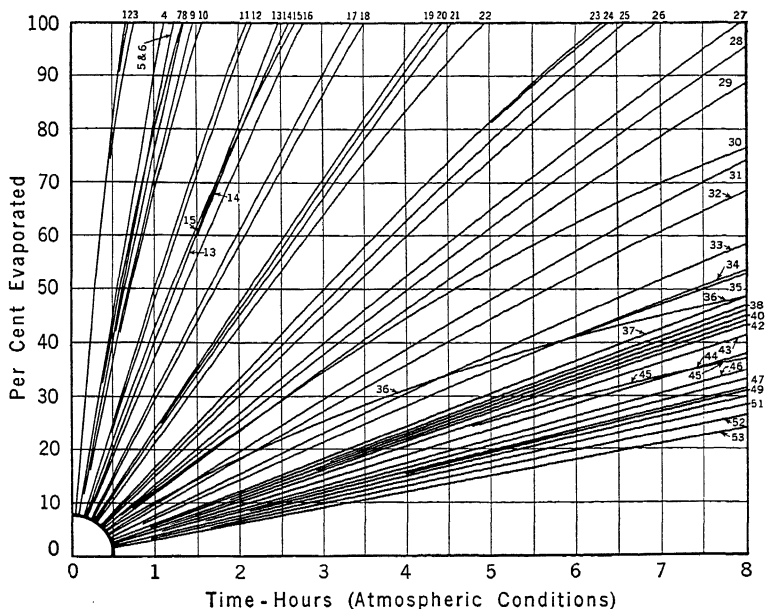
In addition to the above factors, the solvent power or dilution ratio of the solvent must be given consideration. This property has no relation to the boiling point and evaporation rate (3). Solvents which give the minimum viscosity to their solutions and will stand the highest dilution with non-solvents without precipitation are considered superior.

The molecular weight of a solvent indicates to a considerable extent the viscosity to be obtained with a given solution of nitrocellulose in that solvent. For example, a solution of 2 pounds of  $\frac{1}{2}$  second nitrocellulose in 1 gallon of acetone would produce a thin mobile liquid, whereas the same quantity of  $\frac{1}{2}$  second nitrocellulose in amyl acetate gives a decidedly viscous liquid. In general, the solvents having lower molecular weights, such as ethyl acetate, isopropyl acetate, and acetone, produce thinner solutions than the higher molecular weight solvents, such as butyl propionate and butyl butyrate.

### DILUENTS

As previously mentioned, the diluent serves the dual function of acting as resin solvent, which it often performs more efficiently than the nitrocellulose solvents, and as an inexpensive bulking liquid to reduce the lacquer cost. Severe competition necessitates the use of as large a quantity of diluent as possible in most lacquer formulations. The formulator must be careful in the selection of diluents as well as solvents so that during evaporation of the liquids the solvent mixture does not become unbalanced by incorrect proportions of either solvent or diluent. This feature, if not taken into consideration, may cause blushing, either due to precipitation of the nitrocellulose, or resin, or both.

Coal tar distillates are the most efficient of the diluents since they have excellent solvent properties for the resins used in lacquers and

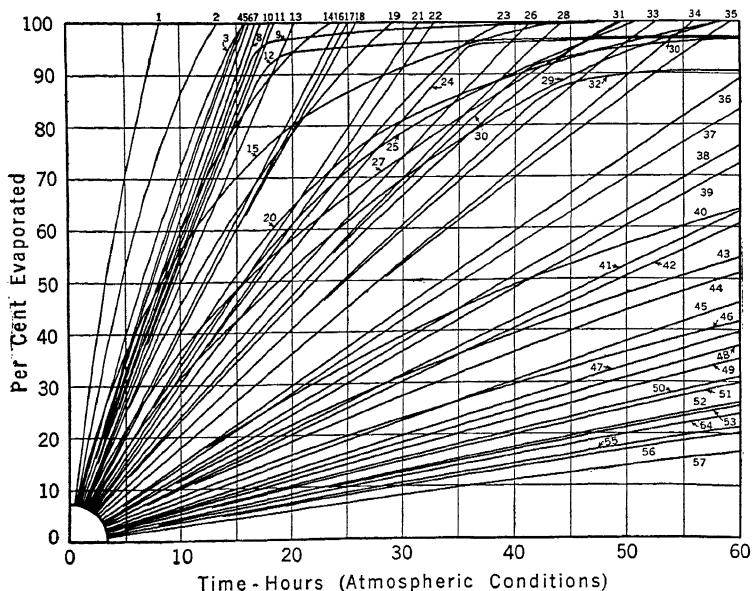


Courtesy of A. K. Doolittle, *Ind. Eng. Chem.*,  
October, 1935 (Vol. 27, No. 10), p. 1170.

FIG. 4. Relative Evaporation Rates of Fast-to-Intermediate-Evaporating Liquids.

1. Methyl acetate	82%	27. <i>n</i> -Butyl acetate	90%
2. Acetone	99	28. Mesityl oxide	86
3. Methylacetone (acetone 48%, methyl acetate 28%, methanol 24%)	..	29. Methyl <i>n</i> -butyl ketone	87
4. Cyclohexane	..	30. Xylene	..
5. Benzene	..	31. Isobutanol	99
6. Ethylene dichloride	99	32. <i>sec</i> -Amyl acetate	92
7. Ethyl acetate	85	33. <i>sec</i> -Hexyl acetate	98
8. Methanol (anhydrous)	99	34. Amyl acetate, mixed isomers	84
9. Methyl ethyl ketone	99	35. <i>n</i> -Butyl propionate	99
10. Isopropyl acetate	95	36. High-flash naphtha	..
11. Ethyl propionate	96	37. Methyl Cellosolve	99
12. Ethanol (anhydrous)	99	38. Dipropyl ketone	99
13. Methyl propyl ketone	99	39. Methyl amyl acetate	95
14. Isopropanol (anhydrous)	99	40. Steam-distilled turpentine	..
15. Diethyl ketone	99	41. <i>n</i> -Butanol	99
16. Petroleum naphtha	..	42. <i>sec</i> -Amyl alcohol	99
17. Toluene	..	43. Gum spirits of turpentine	..
18. Solvesso No. 1	..	44. Methyl <i>n</i> -amyl ketone	98
19. <i>sec</i> -Butyl acetate	82	45. Solvesso No. 2	..
20. Hexone (methyl isobutyl ketone)	99	46. Amyl alcohol, mixed isomers	99
21. Isobutyl acetate	96	47. Methyl amyl alcohol	99
22. Ethyl butyrate	99	48. Cellosolve	99
23. Diethyl Cellosolve	95	49. Methyl Cellosolve acetate	99
24. Diethyl carbonate	91	50. Cyclohexanone	67
25. <i>sec</i> -Butanol	99	51. Isopropyl Cellosolve	97
26. Monochlorobenzene	..	52. Hexyl (2-ethyl butyl) ace- tate	91
		53. Cellosolve acetate	96

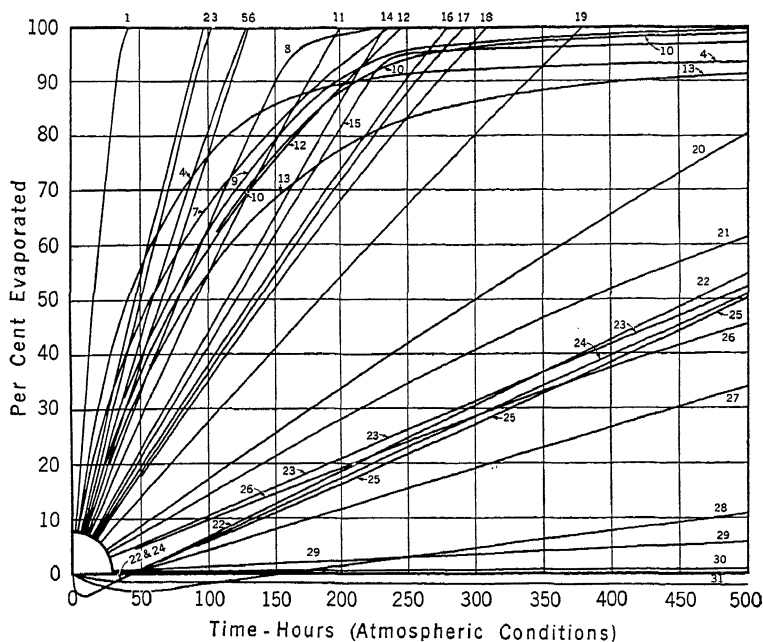




Courtesy of A. K. Doolittle, *Ind. Eng. Chem.*,  
October, 1935 (Vol. 27, No. 10), p. 1171.

Fig. 5. Relative Evaporation Rates of Intermediate-to-Slow-Evaporating Liquids.

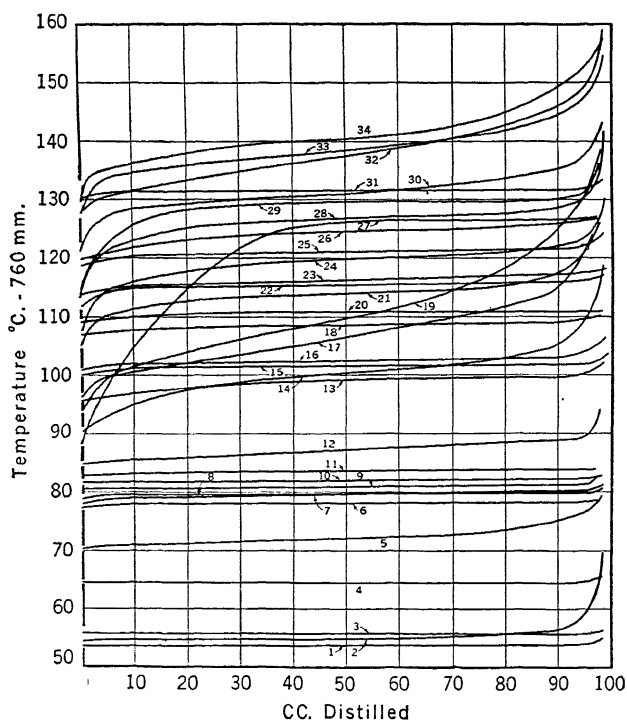
1. <i>n</i> -Butyl acetate	90%	29. Mineral spirits	..
2. Xylene	..	30. Isopropyl lactate	99%
3. <i>sec</i> -Hexyl acetate	98	31. Furfural	98
4. Amyl acetate (mixed isomers)	84	32. Dipentene	..
5. <i>n</i> -Butyl propionate	99	33. <i>o</i> -Dichlorobenzene	..
6. Methyl Cellosolve	99	34. Diacetone alcohol	99
7. Dipropyl ketone	99	35. 3-Methoxy butyl acetate	99
8. Methyl amyl acetate	95	36. Methyl <i>n</i> -hexyl ketone	96
9. Steam-distilled turpentine	..	37. Dichloroethyl ether	99
10. <i>n</i> -Butanol	99	38. Decahydronaphthalene	..
11. <i>sec</i> -Amyl alcohol	99	39. Cyclohexanyl acetate	79
12. Gum spirits of turpentine	..	40. Hercosol	..
13. Methyl <i>n</i> -amyl ketone	98	41. Hexyl (2-ethyl butyl) alcohol	99
14. Amyl alcohol (mixed isomers)	99	42. Fenchone	..
15. High-flash naphtha	..	43. Safe-T-Esso	..
16. Methyl amyl alcohol	99	44. Phorone	..
17. Cellosolve	99	45. Butyl Cellosolve	99
18. Methyl Cellosolve acetate	99	46. Solvesso No. 3	..
19. Solvesso No. 2	..	47. Cyclohexanol	94
20. Cyclohexanone	67	48. Furfuryl acetate	99
21. Isopropyl Cellosolve	97	49. Acetonylacetone	95
22. Hexyl (2-ethyl butyl) acetate	91	50. Tetrahydrofurfuryl alcohol	99
23. Cellosolve acetate	96	51. Diethyl Carbitol	99
24. Ethyl lactate	98	52. Furfuryl alcohol	98
25. Methylcyclohexanone	74	53. Tetrahydronaphthalene	..
26. Butyl butyrate	99	54. Octyl (2-ethyl hexyl) acetate	99
27. V. M. & P. naphtha	..	55. Butyl Cellosolve acetate	99
28. Diisobutyl ketone	95	56. Butyl lactate	97
		57. Glycol diacetate	99



Courtesy of A. K. Doolittle, *Ind. Eng. Chem.*,  
October, 1935 (Vol. 27, No. 10), p. 1175.

Fig. 6. Relative Evaporation Rates of Slow-to-Very-Slow-Evaporation Liquids.

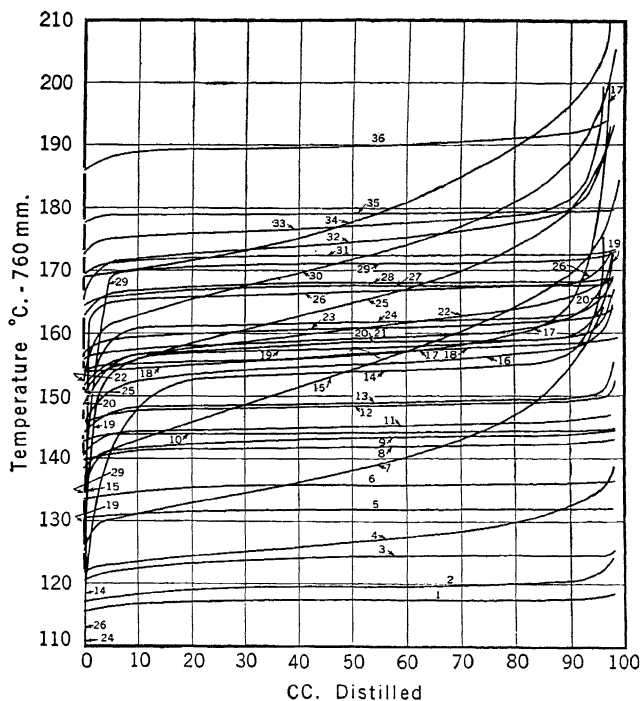
1. Cellosolve acetate	96%	17. Butyl Cellosolve acetate	99%
2. Hexyl (2-ethyl butyl) acetate	99	18. Butyl lactate	97
3. Fenchone	..	19. Glycol diacetate	99
4. Hercosol	..	20. Octyl (2-ethyl hexyl) alcohol	99
5. Phorone	..	21. Pine oil	..
6. Butyl Cellosolve	99	22. Methyl Carbitol	..
7. Safe-T-Esso	..	23. Methyl Carbitol acetate	99
8. Cyclohexanol	94	24. Carbitol	..
9. Furfuryl acetate	99	25. Benzyl alcohol	99
10. Tetrahydrofurfuryl alcohol	99	26. Heavy pine oil	..
11. Acetylacetone	95	27. Carbitol acetate	97
12. Solvesso No. 3	..	28. Butyl Carbitol	96
13. Furfuryl alcohol	98	29. Butyl Carbitol acetate	99
14. Diethyl Carbitol	99	30. Diglycol diacetate	99
15. Tetrahydronaphthalene	..	31. Benzyl Cellosolve	99
16. Octyl (2-ethyl hexyl) acetate	99		



Courtesy of A. K. Doolittle, *Ind. Eng. Chem.*,  
October, 1935 (Vol. 27, No. 10), p. 1176.

Fig. 7. Standard Distillations with Fast-to-Intermediate-Evaporating Liquids.

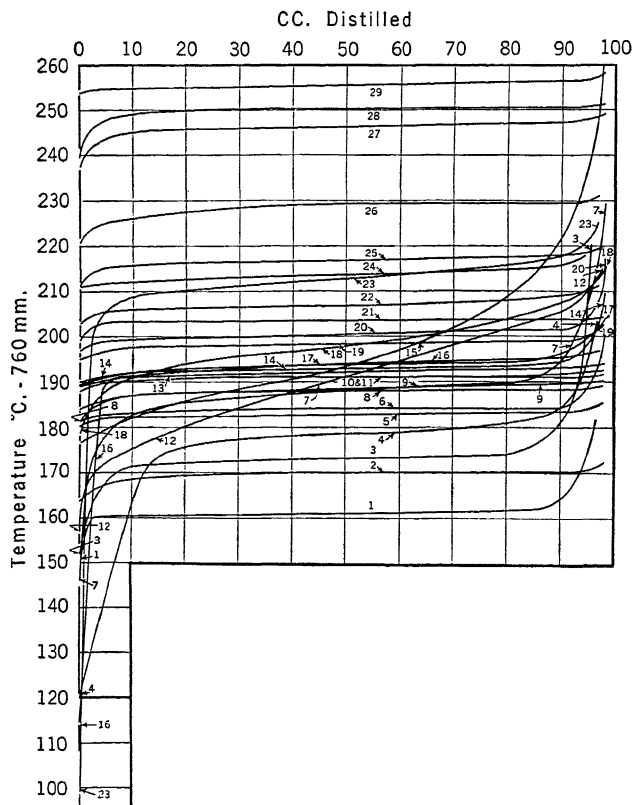
1. Methyl acetate	82%	18. Isobutanol	99%
2. Methylacetone (acetone 48%, methyl acetate 28%, methanol 24%)	..	19. Solvesso No. 1	..
3. Acetone	99	20. Toluene	..
4. Methanol (anhydrous)	99	21. <i>sec</i> -Butyl acetate	82
5. Ethyl acetate	85	22. Hexone (methyl isobutyl ketone)	99
6. Ethanol (anhydrous)	99	23. Isobutyl acetate	96
7. Methyl ethyl ketone	99	24. Ethyl butyrate	99
8. Benzene	..	25. Diethyl Cellosolve	95
9. Cyclohexane	99	26. <i>n</i> -Butyl acetate	90
10. Isopropanol (anhydrous)	99	27. Diethyl carbonate	91
11. Ethylene dichloride	99	28. Methyl <i>n</i> -butyl ketone	87
12. Isopropyl acetate	95	29. Mesityl oxide	86
13. <i>sec</i> -Butanol	99	30. <i>sec</i> -Amyl acetate	92
14. Ethyl propionate	96	31. Monochlorobenzene	..
15. Diethyl ketone	99	32. Xylene	..
16. Methyl propyl ketone	99	33. Amyl acetate (mixed isomers)	84
17. Petroleum naphtha	..	34. <i>sec</i> -Hexyl acetate	98



Courtesy of A. K. Doolittle, *Ind. Eng. Chem.*,  
October, 1935 (Vol. 27, No. 10), p. 1177.

FIG. 8. Standard Distillations with Intermediate-to-Slow-Evaporating Liquids.

1. <i>n</i> -Butanol	99%	19. Cyclohexanone	67'
2. <i>sec</i> -Amyl alcohol	99	20. Isopropyl lactate	99
3. Methyl Cellosolve	99	21. Steam-distilled turpentine	..
4. Amy alcohol (mixed isomers)	99	22. Butyl butyrate	99
5. Methyl amyl alcohol	99	23. Hexyl (2-ethyl butyl) acetate	91
6. Cellosolve	99	24. Furfural	98
7. <i>n</i> -Butyl propionate	99	25. High-flash naphtha	..
8. Isopropyl Cellosolve	97	26. Methylcyclohexanone	74
9. Dipropyl ketone	99	27. Diisobutyl ketone	95
10. Methyl Cellosolve acetate	99	28. Dichloroethyl ether	99
11. Methyl amyl acetate	95	29. 3-Methoxy butyl acetate	99
12. Methyl <i>n</i> -amyl ketone	98	30. Mineral spirits	..
13. Hexyl (2-ethyl butyl) alcohol	99	31. Methyl <i>n</i> -hexyl ketone	96
14. Ethyl lactate	98	32. Cyclohexanyl acetate	79
15. Solvesso No. 2	..	33. Dipentene	..
16. Cellosolve acetate	96	34. V. M. & P. naphtha	..
17. Gum spirits of turpentine	..	35. <i>o</i> -Dichlorobenzene	..
18. Diacetone alcohol	99	36. Decahydronaphthalene	..



Courtesy of A. K. Doolittle, *Ind. Eng. Chem.*,  
October, 1935 (Vol. 27, No. 10), p. 1178.

FIG. 9. Standard Distillations with Slow-to-Very-Slow-Evaporating Liquids.

1. Cyclohexanol	94%	16. Phorone	..
2. Butyl Cellosolve	99	17. Carbitol	..
3. Furfuryl alcohol	98	18. Solvesso No. 3	..
4. Tetrahydrofurfuryl alcohol	99	19. Octyl (2-ethyl hexyl) acetate	99%
5. Furfuryl acetate	99	20. Tetrahydronaphthalene	..
6. Octyl (2-ethyl hexyl) alcohol	99	21. Benzyl alcohol	99
7. Butyl lactate	97	22. Methyl Carbitol acetate	99
8. Diethyl Carbitol	99	23. Pine oil	..
9. Glycol diacetate	99	24. Heavy pine oil	..
10. Acetylacetone	95	25. Carbitol acetate	97
11. Butyl Cellosolve acetate	99	26. Butyl Carbitol	96
12. Safe-T-Esso	..	27. Butyl Carbitol acetate	99
13. Methyl Carbitol	..	28. Diglycol diacetate	99
14. Fenchone	..	29. Benzyl Cellosolve	99
15. Hercosol	..		

the least tendency toward gelation of the lacquer when used in high proportions. These materials comprise in most cases 40 to 50 per cent of the liquid portion of the lacquer, depending upon the method of application and the other ingredients used.

Petroleum diluents are available which are close approximations of the distillation and evaporation ranges of benzol, toluol, xylol, and high-flash naphtha, but these liquids, while lower in price, are not as good resin solvents and also require the use of a larger proportion of the active ester solvents than the coal tar distillates. Although of considerable commercial importance, these straight petroleum distillates are being somewhat supplanted by the high-solvency petroleum fractions. These materials are comparable in solvency to mixtures of coal tar and petroleum distillates, and in general solvent characteristics are somewhere between the two. Since coal tar hydrocarbons vary in production to great extent with the steel mill activity, the advent of substitutes for coal tar distillates with adequate chemical and physical characteristics has filled a long-felt need in the lacquer industry. Moreover, the lower prices of petroleum fractions permit the manufacture of more economically priced lacquers.

## RESINS

Resins are important constituents of modern nitrocellulose lacquers. They perform various functions, some of which are:

1. To increase adhesion, as films made of nitrocellulose alone are notably lacking in this desirable characteristic.
2. To increase body, depth, and solid or non-volatile content without unduly raising the cost, and without changing the viscosity appreciably.
3. To increase gloss, luster, and brilliance.
4. To improve outdoor durability by the use of certain alkyd resins, particularly in clear finishing lacquers.
5. To improve water resistance, chemical resistance, etc., such as necessary under special conditions.

The most suitable resins are those which are soluble in mixtures of esters, alcohols, and hydrocarbons, and give a clear, transparent film, with good permanent gloss.

Adhesion of the film is increased by the use of proper resin or resins and plasticizer combinations; some of the resins are shellac, elemi,

dammar, ester gum and alkyds. Ester gum is generally used in conjunction with other materials so that a properly plasticized film is obtained. A single resin will not always give the desired results so that the lacquer chemist must find out by experimentation what combination of resins, with plasticizers and nitrocellulose, will produce a film that will meet service requirements. For example, for adhesion to bare metal, a different type of formulation is required than for use over a baked or air-dried oil primer.

The requirements of the finished lacquer film govern the selection of resins and plasticizers, as well as the solvents. Resins should be selected which avoid difficulties, such as loss of adhesion, which cause early failure through peeling and scaling, loss of gloss, or lack of water and humidity resistance. In pigmented lacquers, it is essential that the resins have no livering action with the pigments on aging.

Attempts have been made to classify resins and draw some deductions as to their probable effect in a lacquer film. However, experienced lacquer formulators have found that resins, when used in appreciable quantities in lacquer, impart their own physical and chemical characteristics to the lacquer finish. They must be compatible with the nitrocellulose and other ingredients, so that a clear, homogeneous film is formed. For example, addition of soft resins softens the film, hard resins harden it, water-resistant resins improve the water resistance, glossy resins improve the luster, and resins resistant to sunlight and weathering improve the outdoor durability. There may be an occasional exception to the rule. The quantity of resin used in ratio to the nitrocellulose depends upon the film desired, and whether this should have its outstanding characteristics similar to those of the nitrocellulose or similar to the resin or resins employed. The tendency is to use as high a percentage of resin as possible, because of the relatively low cost of the resins and also because of the increased fullness of film, depth of finish, and increased luster which is obtained with a high resin content. It is also important that the lacquer in which a resin is used remain clear on aging.

The proper selection of solvents is particularly important in high-resin lacquers so that there will be no precipitation of either resin or cotton during the evaporation of the solvents, as this would ruin the film. The thinner which is used to reduce the lacquer to the required consistency for application (spraying, dipping, brushing, and other methods) must be formulated so as to blend perfectly and hold all the lacquer ingredients in a clear solution.

## Natural Resins

Natural resins are used to some extent, but the volume has been decreased by the use of synthetic resins.

**Dammar resins** have the lowest acid number of the important natural resins; it varies between 25 to 35 in the commercial grades.

Since dammar is not completely soluble in alcohol and esters used in lacquers, it must be "dewaxed," a process which removes the insoluble portion of the resin and leaves a clear solution known as "dewaxed dammar solution." The dammar is dissolved in a suitable solvent such as toluol, and the  $\beta$ -resene or "wax" is precipitated by the addition of denatured alcohol. The wax-free solution is of low viscosity, about 0.5 poise (a, Gardner-Holdt), and is adaptable to a wide variety of lacquer formulations.

Good results are obtained with the better grades of dammar, by dissolving the resin in an equal weight of toluol, xylol, or other coal tar solvent, and adding an equal weight of denatured alcohol. For the cheaper grades, the toluol is better replaced by a mixture of two-thirds light petroleum naphtha and one-third ethyl acetate, or by ethyl acetate 12.5 per cent, acetone 12.5 per cent, and benzol 75 per cent. By increasing the dammar proportion to as much as two and a half parts, the toluol procedure may be made to give good results with all grades of dammar. The wax is precipitated as a brownish gray mass, which is allowed to settle out from the solution, usually requiring twelve hours or longer. Some operators prefer to have the alcohol in the original toluol solution, claiming it gives more clarity to the final solution, but this method obviously requires a longer agitation in the initial dissolving process. The use of a steam-jacketed kettle for making the dammar solution is also popular; it helps in producing a clear solution which can be drawn off, leaving the wax at the bottom of the mixing tank. A filter press, plate and frame type, is frequently employed to secure a crystal-clear dammar solution. Paper backed up with cloth is the usual filtering medium, and the residue remains in cake form in the press. This method is obviously more efficient and quicker than the older method of settling and decantation. As one of the important characteristics of dammar solutions is paleness, it is important to make the solution in wooden or enameled steel tanks, and store it in wooden barrels, tin- or lead-lined drums, or tanks. Storage in iron or steel containers will give a yellowish or dark amber color to the solution in a short time, and to a lesser extent storage in copper and brass. Although the actual wax content of dammar resin



varies from 8 to 11 per cent, there is usually a loss of 15 to 20 per cent as some of the solution is occluded in the precipitated wax. This wax is sometimes discarded, but it has been found to have valuable properties in certain types of formulations, such as pigmented undercoats, and materials which do not contain much alcohol in the solvent combination.

Dammar is a valuable ingredient in lacquers as it produces a product which may be rubbed and polished with ease to a high gloss. It was used extensively in furniture and automobile lacquers until the advent of synthetic resins, which replaced dammar to a certain extent.

**Gum Elemi.** Gum elemi is a soft colorless resin. It is of semi-solid or waxlike consistency and at ordinary temperatures is a soft, sticky mass. It has a pleasant and balsamic odor which remains to some extent in the film. It has the property of retaining flexibility over a long period of time and, owing to its soft sticky nature, can be used only in limited amounts in lacquers. It is soluble in coal tar solvents. Wood fibers and other impurities which are retained in the resin must be removed by straining or filtering after dissolving in toluol. Its principal use is in metal lacquers, silver lacquers, and bronzing liquids, where it imparts adhesion and flexibility but decreases hardness. The use of gum elemi is limited to some extent because of the tendency of the film to yellow on aging.

**Shellac.** Both orange and bleached white shellac contain approximately 5 per cent wax, which is undesirable for use in lacquers. A dewaxed grade of shellac, known as refined white shellac, is manufactured for use in the lacquer industry and is usually sold in four-, six-, or eight-pound cuts dissolved in anhydrous alcohol. The above solutions are clarified by centrifuge, settling, or filtration and then stored in wooden tanks for at least three months. This storage produces a very clear solution, and the aging of the solution increases the compatibility of the shellac with nitrocellulose. Since shellac is only slightly soluble in ester solvents and hydrocarbons, great care must be used in selecting proper solvent combinations to avoid precipitation in a lacquer. In general, a solvent blend of high alcoholic content is desirable. Also the use of higher boiling alcohols, such as butyl alcohol, is advantageous.

The addition of shellac to a nitrocellulose lacquer improves adhesion and hardness, increases the luster, but decreases the water and moisture resistance as well as the drying time. Because of the inherent property of shellac to retain solvents, the quantity of shellac used in a lacquer is limited. Refined dewaxed shellac is often used to advantage in

metal lacquers, where it provides gloss and adhesion as well as toughness. Also, because of its comparative rapid drying and excellent sealing qualities, shellac had been extensively used in the furniture industry as a sealing coat over the stain and wood filler. However, since the manufacture of lacquer sanding sealers, these have largely replaced shellac owing to their faster drying properties, easier sanding, and better compatibility with the lacquer finishing coats. Thus, a straight lacquer finish is obtained, eliminating the use of shellac.

### Synthetic Resins

The use of synthetic resins in lacquers has increased remarkably in recent years.

**Ester Gum.** Ester gum is the first synthetic resin to be used in lacquers. A number of commercial grades are available, with acid numbers of 2, 4, 6-8, etc., and with varying degrees of hardness, color, and solubility. Ester gum is pale in color. It is unaffected by water, hot or cold, but is hydrolyzed by hot alkalis. It is soluble in coal tar solvents, ester solvents, and the usual solvent combinations found in nitrocellulose lacquers. It is the cheapest resin used in lacquers, and is used in large quantities.

For use, ester gum is dissolved in mixtures of 60 per cent toluol and 40 per cent ethyl acetate by volume, in the proportion of 6, 8, or 10 pounds to the gallon. Such solutions can be blended with nitrocellulose solutions without danger of precipitation. Ester gum goes into solution readily, and any type of agitator mixer can be employed. If paleness of color is desired, the solution should be stored in tin-lined tanks or drums or wooden barrels, as iron and steel containers cause discoloration.

Ester gum is used in lacquers in large proportions along with properly selected plasticizers, and also in conjunction with dammar, shellac, and numerous synthetic resins. It imparts gloss and body to the finish, at the same time decreasing the raw material cost. Higher percentages of ester gum can be used in interior finishes than in those for outdoor use. In pigmented enamels, owing to additional hardness imparted to the film by the pigments, as much ester gum as two or three times the weight of cotton can be used, with proper plasticizers.

**Alkyd Resins.** Alkyd resins as used in nitrocellulose lacquers are principally of the glycerol-phthalic anhydride type, modified with either drying or non-drying oils. A large number of commercial grades are available, which in general possess the advantage of permitting a high resin to cotton (nitrocellulose) ratio without loss of durability.

In some cases, particularly in clear lacquers, the addition of alkyd resin improves the outdoor durability, because such a film is less affected by the actinic rays of sunlight than is a film of nitrocellulose alone, or films of nitrocellulose admixed with other types of resins, such as dammar, ester, or copal.

In the soft or non-drying alkyds, castor oil or its derivatives are generally the modifying agents used in manufacture of the resin, and  $2\frac{1}{2}$  to 3 parts resin to 1 part cotton is found to be the maximum ratio.

When drying types of alkyds are used, the addition of small amounts of metallic driers accelerates the drying and hardening of the resin, so that the amounts of resin can be still higher, as 4 to 5 parts resin to 1 part nitrocellulose. These finishes are susceptible to lifting action in a multicoat system, so that their use is limited to one-coat finishes, or where a baking process can be employed to carry the drying process beyond the stage where it is lifted by the lacquer solvents of the next coat.

Alkyds of this type are pale in color, and, where unusually pale-colored resins are necessary, such as in white enamels for refrigerator finishing, special resins made from soybean oil derivatives and other non-yellowing oils are employed. The alkyds also impart improved adhesion, grease resistance, and flexibility retention to lacquers. Because some of the alkyds have higher acid numbers, pigmented enamels should be formulated to contain the minimum of basic pigments, to avoid difficulties from livering.

The modified alkyds are in general of the hard, brittle type, which have high melting points, hardness of film, and low solvent retention; that is, they permit rapid evaporation of the solvents, with fast surface and through drying of the film.

The maleic type of alkyd resin finds wide use in wood sealers and wood finishing lacquers, owing to its relatively low viscosity in solutions of high concentration, ability to release solvent rapidly on drying, pale color, excellent gloss, and good durability. This type of resin also has good moisture and alkali resistance, levels well, and gives a full-bodied appearance to the film. It is used alone and in conjunction with ester gum to produce wood and metal lacquers, which dry rapidly and stand sanding, rubbing, or polishing. This type of lacquer also has good alcohol resistance. Outdoor durability of lacquers made with this type of resin is not so good as with the soft flexible alkyds, but is comparable to the other synthetic resins of the hard, brittle type, and natural resins such as dammar.

**Phenolic resins**, in general, give excellent water and moisture resistance, acid and alkali resistance, as well as adhesion. Certain types are suitable for clear outdoor metal and finishing lacquers, where the resin provides added durability, color retention, and tarnish resistance to the lacquer finish.

**Urea-formaldehyde resins** are converted by heat into a very hard, tough, and chemically resistant coating. Since the resin alone is too brittle for use in coatings, it is often combined with more flexible resins, such as alkyds, and is also suitable for use in nitrocellulose lacquers. It is generally recommended that the film be baked or forced-dried for 1 hour at 250° F. The urea resin together with a plastic alkyd and proper amounts of cotton can be formulated into a baking lacquer with excellent paleness of color, good color retention, hardness, mar resistance, alcohol resistance, and adhesion.

**Vinylite resins** also are available for use in nitrocellulose lacquers, and impart qualities of pale color, color retention, and water and chemical resistance to the lacquer. Special primers are necessary to secure adhesion of this type of finish to metallic and other surfaces, and special solvents and plasticizers are also required. This finish is also baked to secure maximum properties of durability inherent in the vinylite resin.

**Acryloid resins** are colorless flexible resins, of varying degrees of hardness, and are suitable for use as film-forming materials by themselves. Combinations of acryloid resins with nitrocellulose or cellulose acetate are also of interest, owing to excellent color retention on exposure to sunlight, excellent adhesion on most surfaces, water-white color, unusual extensibility, similar to rubber, and high resistance to water, alcohol, acid, mineral oils, greases, fumes, vegetable oils, and animal fats.

## PLASTICIZERS

Plasticizers serve to improve the lacquer film in numerous ways. Their main purpose is to improve the flexibility of the film, thus increasing its durability under adverse conditions. The nitrocellulose film without plasticizer is brittle, cracks easily, and has a decided tendency to shrink and pull away from the surface to which it is applied. A properly plasticized film will resist the severe variations of temperature when exposed to the elements, and will retain its elasticity indefinitely. To obtain certain desired results, however, it is necessary to gage properly the amount of plasticizer to be used when

formulating a product, since it is often advisable to limit the degree of elasticity.

Plasticizers for nitrocellulose were discovered about seventy years ago (4, 8), when camphor was found to be a solvent for nitrocellulose and to impart elasticity to the resultant product. However, camphor was found to evaporate from the mixture, and other more suitable plasticizers were developed. A great number of plasticizers have been placed on the market, and the number is steadily growing (6, 11).

Plasticizers may be grouped as mobile liquids, oils, and resins. Each serves its own special purpose, and the lacquer formulator uses them as the occasion demands. A satisfactory plasticizer must comply with a number of rigid requirements which may be listed as follows:

1. Compatibility with nitrocellulose and resins.
2. Solubility in lacquer solvents.
3. Permanent flexibility due to non-volatility.
4. Low moisture permeability.
5. Lack of residual odor.
6. Non-yellowing on prolonged aging.
7. Improved final film leveling.
8. Chemical stability.

Oils, such as raw and blown castor, blown rapeseed, blown soybean, and specially processed linseed are largely used to impart plasticity to lacquer films. As the oils are generally considered to be dispersed throughout the film in the form of minute globules, they are not as efficient in plasticizing effect as the chemical plasticizers which are nitrocellulose solvents. The chemical plasticizers have less tendency to sweat or spew out of the film under heat, have less odor, greater stability, and, though usually more expensive than the oils, they are used in considerable volume.

Castor oil, because of its non-oxidizing properties and low cost, is the most popular oil for lacquer use, while dibutyl phthalate and tricresyl phosphate are the most popular chemical plasticizers. A combination of two or more plasticizers often gives desirable film properties, such as equal parts of castor oil and dibutyl phthalate. Blown soybean oil is rapidly increasing in acceptance as a lacquer plasticizer, giving best results when used along with other plasticizers, as castor oil, dibutyl phthalate, or tricresyl phosphate. This oil has the advantage of being domestically grown and refined, and is available at low cost.

The plasticizers in this table are among those most commonly used in the lacquer industry.

LACQUER PLASTICIZERS (11)

Chemical Name	Trade Name	Boiling Range	Specific Gravity	Flash Point
Benyl benzoate	Ergol Perudin	323° C.	1.125 20°/20° C.	148° C.
Butyl acetyl ricinoleate	Baker's P6			
Butyl phthalyl butyl glycolate	Santicizer B-16	219° C. 5 mm.	1.098-1.100 25° C.	
Butyl stearate		220-360° C. 25 mm.	0.855-0.857 25° C.	145° C.
a Camphor		209° C.	0.990 25° C.	Melting range 179° C.
a,B Camphor		Melting range 174° C.		
Diamyl phthalate		344° C.	1.023 20°/20° C.	159° C.
Dibutyl phthalate		195-200° C. 5 mm.	1.043-1.050 20°, 15° C.	160° C.
Dibutyl tartrate		300° C. ca.	1.064-1.091	157° C.
Dibutoxy ethyl phthalate	Apex No. 1	233° C. 5 mm.		
Tributyl phos- phate		180° C. 20 mm.	0.979 20°, 4° C.	
Tributyl citrate		210-226° C. 8 mm.	1.045 20° C.	200° C.
Tricresyl phos- phate	Lindol	235-265° C. 5 mm.	1.18 15.5° C.	190° C.
Triethyl citrate	Adinol	294° C.	1.1369 20° C.	
Triphenyl phos- phate	Altal	368° C. 20 mm.	1.185	214-235° C.

PIGMENTS USED IN LACQUERS

Pigments, or dyes, are incorporated in lacquers to give the desired color. Here we note a marked difference between oleoresinous paints and enamels and lacquers. Whereas an average paint might contain six or eight pounds of pigments to a gallon, an attempt to use an equal amount in a lacquer formula would give a product of poor

durability and no adhesion (12). The high volatile content of lacquers as compared with oleoresinous materials shows that there is less binder to hold the pigment particles together. Thus the pigments used in lacquers are somewhat different from those used in other types of finishing materials. In general, the pigments of greatest strength and hiding capacity and low oil absorption give best results. Pigments besides imparting color to lacquer also serve to protect it for exterior use by preventing penetration of the actinic rays of sunlight, which cause rapid decomposition and disintegration of a clear nitrocellulose film. Pigments of high opacity enable the production of automotive and other exterior lacquer enamels which surpass in durability the best exterior oleoresinous and synthetic paints and enamels.

### White Pigments

**Titanium dioxide**, because of its high opacity, is of most importance among white pigments used in nitrocellulose lacquers. As little as six to eight ounces per gallon can be used, and the low oil absorption grades are most suitable. Although the titanium dioxide alone can be used for interior enamels, for exterior purposes it must be used in combination with other pigments such as zinc oxide and antimony oxide, which decrease the excessive chalking of enamels pigmented with titanium dioxide alone. Non-chalking titanium dioxides have recently appeared on the market, which are a decided improvement over the previous type.

**Titanium barium pigment** is also used to some extent in interior and exterior white lacquer enamels and also in tints, such as ivories, fawns, and grays. This pigment used alone to produce white enamels shows less tendency toward excessive chalking on exterior exposure than the pure titanium dioxide pigment.

**Titanium calcium pigment** is not recommended for use in exterior finishes but is employed to advantage in flat white lacquers, undercoaters, primers, and surfacers. Its low specific gravity and consequent non-settling characteristics together with low cost contribute to its interest for use in lacquer requiring higher pigment bulk.

The titanium pigments as a class are chemically inert, of high opacity, and have minimum after-yellowing properties. Properly ground, they contribute smoothness and uniformity to the enamel and improved flow and leveling as compared with the more reactive pigments. Their high opacity permits manufacture of white and light tint enamels having high coverage per coat on application, with resultant economy in finishing costs.

**Zinc Oxide.** This pigment is used in lacquer enamels, usually in combination with titanium dioxide or other pigments. Although a number of grades are available, the French process material is of most importance for lacquer use. Though of less opacity than the titanium pigments, it has some stabilizing influence on the exterior white enamels and contributes to reduction of chalking tendencies of the titanium pigmented finishes. It produces finishes of good gloss and luster, smoothness, and a brilliant white color. Certain tints of delicate color are produced with zinc oxide in combination with other colored pigments, which are cleaner and more brilliant in tone than can be secured by use of other white pigments.

**Antimony Oxide.** This white pigment has been used because of its non-chalking and brilliant white character. It is excellent for exterior lacquer enamels, where it is used alone or with zinc oxide and titanium dioxide to decrease the chalking tendencies. It is not affected by sulfur fumes in the presence of zinc oxide and thus has good color retention on exposure when used in combination with zinc oxide. Although antimony oxide is not used extensively in the United States, it has become quite popular abroad and finds some application in special problems where other white pigments are not satisfactory.

**Zinc Sulfide and Lithopone.** These pigments, varying from technically pure (98 per cent) zinc sulfide to lithopones of 50 per cent zinc sulfide and 50 per cent barium sulfate, depend for their opacity on the presence of zinc sulfide. They are used principally in interior enamels for industrial applications, also for architectural enamels. The high refractive index and hiding power enable production of finishes with desirable characteristics. The cheaper grades of lithopone are also used in flat white lacquers, surfacers, and undercoats.

### Extenders

**Barytes-blanc fixe** are principally barium sulfate; they may contain traces of iron, which may yellow the color of the enamel on aging. They are seldom used in nitrocellulose lacquers.

**Whiting** has little or no tinting value, and is used as a filler and flattener. It adds bulk to sanding surfacers and knifing putties, as well as filling and adhesion properties. Its alkalinity neutralizes traces of free acid which may be present in the solvents, but this same alkalinity makes its use objectionable with such colors as prussian blue and chrome green, as it would accelerate chalking and fading of the color.



**Asbestine**, which is silicate of magnesium and fibrous in structure, and **talc**, which is finely ground and sifted soapstone and flaky in structure, are both used as fillers, extenders, and flattening agents in lacquer enamels. To some extent, they also buoy up heavier pigments and keep them from settling hard in the package. Although very similar in chemical composition, they differ in physical properties as well as in origin. They are used principally in flat and satin finish enamels, undercoats, sanding surfacers, primers, and fillers.

**Silica and Silex.** These extenders are silicon dioxide—the silica usually made from quartz and the silex from flint. They are inert and unaffected by water or chemicals, and are also quite transparent. The grades used in lacquers are purified, finely ground, and air-floated or water-floated. Because of their angular, crystalline structure and extreme hardness, they find useful application in wood fillers, primers, and surfacers. Silica is supposed to improve adhesion on wooden and metallic surfaces because of the surface-roughening effect of the finely divided crystals of angular silica.

### **Carbon Black**

Carbon blacks are used extensively in making black lacquer enamels. A large variety of black pigments of this type are available. In general, carbon blacks are the blackest pigments known, and give highest covering capacity or opacity with the least amount of pigment. Some of the most jet-black carbon blacks are extremely sensitive to conditions of grinding and dispersion, so that often many difficulties are encountered in securing a satisfactory smooth, finely ground paste, which is free from gritty or seedy particles. Research and development work on the dispersion of carbon black for use in nitrocellulose lacquers has resulted in the production of so-called chip black pastes or pigment bases, which provide the maximum jetness of black tone without the use of organic dyes. This is important in the production of automotive and other high-grade black lacquers where durability of color on exterior exposure is essential. It has long been known that black is the most permanent color in finishes, owing to the permanence, non-fading, and chemical inertness of carbon black and also to its non-bleeding characteristics.

The "chip" blacks and pastes are dispersions of highly refined carbon blacks, in mixtures of nitrocellulose and plasticizer, of which the following is a representative formula:

Carbon black .....	13.3%
Nitrocellulose .....	66.7%
Plasticizer .....	20.0%

A black lacquer enamel is made by dissolving chips in lacquer solvents, to which the desired amount of resins (in form of resin solution) and plasticizers is added to produce the finished enamel. Some time, usually two or more hours, of constant agitation is required to produce a satisfactory solution of chip blacks.

Sometimes, when the chips were stored for an extended period of time before being made into finished black lacquer, it was noticed that a loss of depth and brilliance of blackness occurred. This led to the development of black pigment pastes. These pastes carry various concentrations of carbon black, and are quickly and easily converted into finished black lacquer enamels. They are stable in color and other physical properties, unaffected by age or temperature variations, and minimize the fire and explosion hazard present in dry chips. Formulations must be carefully controlled, as there is a tendency for the pastes to gel on long storage, owing to the extreme reactivity of jet-colored carbon blacks.

The black lacquer enamel is made by preparing a solution of the nitrocellulose, resin, plasticizer, and solvents required in the formula, and, when these are thoroughly mixed, adding the black paste to the solution while continuing the agitation. After a uniform dispersion is secured, the lacquer should be centrifuged or filtered.

A representative black paste formula is:

Carbon black .....	6.7 % by wt.
½ second nitrocellulose .....	33.3 %
Dibutyl phthalate .....	10.0 %
Ethyl acetate .....	18.75%
Butyl alcohol .....	3.75%
Butyl acetate .....	2.50%
Toluol .....	25.00%

Weight per gallon—8.7 lb.

This is made into a finished black lacquer enamel by using the following formula:

Dissolve 105 lb. ½ second wet nitrocellulose in solvent mixture composed of:

38.0 gal. toluol
14.0 gal. butyl acetate
4.0 gal. butyl alcohol

Then add:

- 12.0 gal. resin solution (50% solids in toluol)
- 2.5 gal. blown castor oil
- 1.0 gal. dibutyl phthalate

Mix all, then add 200 lb. black paste.

Yield—104 gal.

When the nitrocellulose is completely in solution, add the resin solution, castor oil, and dibutyl phthalate in the order named; then mix in 200 pounds of black paste of the above type, continuing agitation until complete dispersion is secured. Then centrifuge or filter. This will give an exterior lacquer enamel of deep jet-black color, good durability, and flexible film characteristics.

Many variations in formula are possible according to the resins used and the purpose for which the lacquer is intended. Where greater gloss or sheen is required, the resin content can be increased; and, if less gloss or a dull finish is desired, this is accomplished by addition of a pebble mill black base.

Other black pigments, such as lampblack, bone black, black iron oxide, and mineral blacks, are seldom used in making black lacquer enamels but find application in certain tints and blended colors, such as grays, buffs, and browns, and also in lacquer primers, surfacers, and fillers.

Black dyes, such as nigrosine, are used in some special applications but have a tendency to bleed when a lighter color is applied over them as a striping or contrasting color.

### Blue Pigments

**Chinese blue and prussian blue** are used to considerable extent, the former being generally preferred owing to the lesser tendency toward bronzing. These pigments are hard, brittle, and difficult to grind, and they have high oil absorption. Much study and much research by dry color manufacturers have resulted in production of special chinese blues for lacquer use, which when carefully ground in proper vehicles result in blue lacquers of pleasing shade, good color permanence, and minimum bronzing tendency.

**Phthalocyanine blue** is a newly developed blue pigment. While much more expensive per pound than other blue pigments, it has the advantage of greater permanence in both deep blue and tints.

**Ultramarine blue** is available in a variety of shades, and has a beautiful brilliant blue tone. It is resistant to heat and light, but is

readily decomposed by acids, and fairly stable to alkalies. Being more transparent than chinese blue, it finds its principal use in mixed colors and tints.

### Yellow Pigments

**Chrome yellows** are available in many shades, from light and medium to dark or orange chrome. They are soft pigments, easily ground, have good opacity and low oil absorption. Since they contain lead, use with sulfur-containing pigments, such as ultramarine and lithopone or zinc sulfide, should be avoided.

**Cadmium yellows**, or **cadmium sulfide**, are available in shades from lemon-yellow to orange-red, and have good opacity, stability, and color brilliance. They are excellent for use in high-grade lacquer enamels, but their high cost prevents popular use.

**Ferrite yellows** are chemically produced ferric oxides. They have good hiding and tinting strength, but their lack of brilliance limits their use to tints and blended colors.

**Zinc yellow**, or **zinc chromate**, has a delicate greenish yellow tone, and is fast to light. It is much more transparent than other yellows, has less tinting power, and is used only where chrome and other yellows are not permitted. It finds considerable use in metal primers and undercoats, owing to its corrosion-inhibiting properties.

**Hansa yellow** is a yellow dye lake, possessing great brilliance, and is used in special instances where other yellows are not suitable.

### Red Pigments

**Iron oxide reds** are principally ferric oxide,  $\text{Fe}_2\text{O}_3$ , containing varying amounts of alumina and silicate or carbonate of lime. In general, the higher oxide-containing pigments possess higher covering capacity and greater tinting strength.

**Indian red** is used extensively in primers and enamels, also for tinting purposes. It comes in shades of yellowish red to bluish or purple red.

**Spanish oxide** is the reddest and purest of the natural oxides. It is low in price, and extensively used in primers and undercoats.

**Tuscan red** is a combination of Indian red and alizarine lake, which provides a pigment of greater brilliance and depth of color, although with lessened opacity and tinting strength.

The iron oxide reds, when used in tinting white lacquer enamels to pink, flesh, tan, and other shades, have the advantage of being non-

bleeding, so that finishing or striping colors will not be discolored, as would occur if a bleeding red were used in producing the tint. The oxides are hard to grind, but their advantages and low cost make them among the widely used pigments.

**Para red** in the toner or pure form is generally used in lacquers. It is fairly permanent to light, has good opacity, and high tinting strength. However, it bleeds in lacquer solvents, which limits its use to some extent. It has a bluish red tone, is soft, and grinds easily.

**Toluidine red** toner is widely used in lacquers. It has high opacity and tinting strength and good light fastness. It has less bleeding tendency than para red, and is lighter and more brilliant in shade. Toluidine is about the best and most widely used bright red pigment.

**Lithol red** has a bluish cast, somewhat like para red, and with less bleeding tendency. It is used to some extent in specialties where toluidine and para reds are not suitable.

**Cadmium reds** have good hiding and tinting strength and good color stability. Lack of brilliance and high cost limit their use in lacquers.

**Maroon pigments** vary from tuscan reds to alizarine and madder lakes. Much research on the part of dry color manufacturers has resulted in the development of a wide number of lake and dye pigments, which range in shade from deep reddish colors to the dark purples. Hiding capacity and lightfastness are satisfactory with many of these, and many attractive maroon lacquers are now produced which a few years ago were impossible. They lack the opacity of other popular colors, so that great care and caution are necessary in formulating exterior lacquer enamels with these pigments. The maroons still remain the most expensive pigments.

### Green Pigments

**Chrome greens** are extensively used in lacquers. They have good coverage and are fairly stable to light, but are discolored by acids, alkalis, and sulfur.

**Chromic oxide greens** are the most light-fast green pigments. These greens have good heat stability, weather, and chemical resistance. Since they are relatively expensive, they are used only where chemical and light resistance are desired.

**Green lakes** are available in various types and a range of shades. The Hansa types have vivid brilliant colors with fair lightfastness, and are suitable for brilliant shades of lacquer enamels for special industrial applications.

### Brown Pigments

**Siennas.** Raw sienna is a light orange-brown color, whereas burnt sienna is a darker brown. These pigments give dull shades, and are commonly used for blended shades and certain tints.

**Umbers.** Raw umber has a brown color with greenish undertone; the burnt umber has a rich reddish brown color. Umbers have good color permanence, and are often blended with other pigments. Olive greens are produced using umber as the principal pigment and tinting to the desired shade with ferrite yellow, bone black, green, or other pigments.

**Oxide browns** are treated iron oxides which are available in a variety of light to dark brown shades. These materials, in general, have good opacity, color permanence, and tinting strength.

### Flatting Pigments

**Aluminum stearate** is a translucent pigment, which is used to add to clear lacquers to produce a dull or rubbed finish. It is highly water resistant, light in gravity, and a small amount of it produces a marked flatting effect. The pigment is usually ground into a paste and added to the clear lacquer with constant agitation.

**Zinc stearate** is less transparent than the corresponding aluminum compound. It finds widespread application in lacquer sanding sealers, owing to its property of imparting easy sanding qualities to the sealer. Such lacquer sanding sealers have largely replaced shellac as a lacquer undercoat in furniture finishing systems, particularly where speed of production necessitates a minimum period of drying time between application of the sealer and the sanding operation.

**Magnesium silicate** is also used as a flatting pigment, but is less transparent than the aluminum and zinc stearates. It finds advantageous usage in pigmented lacquer enamels and undercoats, where a dull or matt finish is required. See Chapters 18 and 28, Volume II, for other flatting agents.

**Palmitates** of aluminum and zinc are used in much the same way as the stearates to produce flat and dull finish clear lacquers for furniture finishing.

### CLEAR LACQUERS

Clear lacquers may be divided briefly into wood lacquers and metal lacquers. This classification may often overlap and furthermore may be divided into many subdivisions. Generally speaking, wood lacquers are characterized by comparatively high solids; metal lacquers by their toughness and adhesion.

The introduction of low-viscosity cotton revolutionized the finishing of furniture. Until 1922 all transparent finishes were obtained by the use of shellac as a sealer and varnish as the finishing coat. Although shellac is still frequently used, owing to certain features of economy, varnish has been largely replaced by lacquer. Whereas formerly high-grade furniture required two weeks to route through the finishing room, the time has been cut to two days by the use of lacquers. Neither the durability of the finish nor its beauty was sacrificed by this change.

The customary lacquer procedure in the finishing of furniture is the application first of a coat of lacquer sanding sealer, sanded within one hour with dry sandpaper, then two coats of lacquer, with one to two hours between coats. The lacquer may be rubbed the following day, and then the finished articles are ready for packing and shipping.

### Lacquer Sanding Sealer

A lacquer sanding sealer is usually formulated to have 17 to 27 per cent solids at spraying viscosity. The sealer must dry sharply, so that the surface may be dry-sanded with 6-0 Garnet paper with no sign of clogging the paper, as clogging would cut ridges in the film. The film must be hard and firm so that it will support the finishing coats without sinking. It must be sufficiently elastic to withstand the changes of temperature and the stresses formed by the subsequent coats.\*

To obtain fast drying of the sealer coat, it is important that high-melting resins be used, especially those which have a quick solvent release. The solvent portion of the lacquer must evaporate quickly without the retention of any heavy end points. Zinc stearate and magnesium carbonate, when incorporated in the sealer, improve the sanding properties. Magnesium carbonate, because of its opacity, is used only in very small amounts, where increased filling properties are desired. The film should not be too highly plasticized, as this will slow down the drying time and will not improve the quality of the finish. Ease of sanding is desired, but care must be taken that it will not sand through too readily and mar the foundation.

\* It has been found through cold check tests (see page 541) that the degree of elasticity of the sealer coat must be very close to that of the finishing lacquer to obtain the greatest degree of durability and resistance to temperature change.

## FORMULAS

## LACQUER SANDING SEALER

(Low-Viscosity Type)

58 lb.	½ second nitrocellulose wet with 35% ethyl alcohol
62 lb.	30% solids zinc stearate paste
113 lb.	Maleic resin (solid)
19 lb.	No. 15 blown castor oil
12 gal.	Ethyl acetate
21 gal.	Butyl acetate
8 gal.	Butyl alcohol
15 gal.	Toluol
15 gal.	Petroleum naphtha

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100 gal. Yield

Viscosity—26 seconds at 70° F., using No. 4 Ford cup

Total solids—27.00%

## ZINC STEARATE PASTE

18% by weight	Zinc stearate
6.5% by weight	5 second R.S. cotton (dry)
3% by weight	Magnesium carbonate
2.5% by weight	Blown castor oil
16% by weight	Ethyl acetate
6% by weight	Butyl acetate
16% by weight	Ethyl alcohol
32% by weight	Petroleum naphtha

30% solids

## LACQUER SANDING SEALER

(High-Viscosity Type)

28 lb.	5-7 second nitrocellulose wet with 35% ethyl alcohol
60 lb.	30% solids zinc stearate paste
60 lb.	Maleic resin
10 lb.	No. 15 Blown castor oil
24 gal.	Butyl acetate
15 gal.	Ethyl acetate
18 gal.	Toluol
20 gal.	Petroleum naphtha
5 gal.	Butyl alcohol

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100 gal. Yield

Viscosity—25 seconds at 70° F., using No. 4 Ford cup

Total solids—17.00%



### Furniture Wood Lacquers

Furniture lacquers are formulated to produce gloss, semi-gloss, and flat finishes. Gloss wood lacquers are the most commonly used and constitute the largest volume. The prime requisites of a good gloss lacquer are:

1. Good flow or leveling.
2. High solid content or build.
3. Ease of rubbing and polishing.
4. Print resistance.
5. Durability or cold check resistance.
6. Gloss retention.
7. Water and alcohol resistance.
8. Color retention.

If all the above characteristics could be combined in one product, it would be the ideal lacquer. Unfortunately, it is necessary to compromise on those features which are desired most by the prospective buyer.

The durability of a wood lacquer depends upon type and amount of nitrocellulose, resin, plasticizer, and solvents used. The resin must be durable and must be compatible with nitrocellulose; one to three parts of resin to one part of nitrocellulose are generally used. The type of plasticizer must be carefully selected; approximately 30 to 50 per cent of the weight of nitrocellulose is general practice. The solvent must be properly formulated so that it deposits a homogeneous film, holding all the solid ingredients in solution as the solvent evaporates.

Gloss retention refers to the lacquer retaining its original gloss on aging. Certain types of resin and plasticizer will dull as they progressively deteriorate. A chemically inactive resin should be used and also a non-volatile plasticizer, so that exposure and wear will have little effect on the gloss and other original characteristics of the film.

The solid content of wood lacquers at spraying consistency, which largely determines the build on the wood surface, may vary from 12 to 35 per cent. This will depend on the viscosity of the nitrocellulose, the type and viscosity of the resin and plasticizer, as well as the solvent composition of the lacquer.

The ease of rubbing and polishing of the lacquer coat is of great importance. The lacquer must rub and polish easily, with no drag on the rubbing pad. It must polish to a sharp high gloss.

**Cold Check Test.** For the past five years the furniture, radio cabinet, and piano industries have used a cold check test to determine

## FORMULAS

## GLOSS WOOD LACQUER

(Low-Viscosity Type)

- 57 lb.  $\frac{1}{2}$  second nitrocellulose wet with 35% ethyl alcohol  
 118 lb. Maleic resin  
 16 lb. Non-oxidizing long-oil alkyd  $\left\{ \begin{array}{l} 60\% \text{ solids} \\ 40\% \text{ toluol} \end{array} \right.$   
 21 gal. Ethyl acetate  
 16 gal. Butyl acetate  
 8 gal. Butyl alcohol  
 15 gal. Toluol  
 16 gal. Petroleum naphtha
- 
- 100 gal. Yield

Viscosity—25 seconds at 70° F., using No. 4 Ford cup

Total solids—27.00%

## GLOSS WOOD LACQUER

(High-Viscosity Type)

- 24 lb. 5-7 second nitrocellulose wet with 35% ethyl alcohol  
 146 lb. Maleic resin  
 20 lb. Non-oxidizing long-oil alkyd  $\left\{ \begin{array}{l} \\ \end{array} \right.$   
 21 gal. Ethyl acetate  
 14 gal. Butyl acetate  
 7 gal. Butyl alcohol  
 18 gal. Toluol  
 20 gal. Petroleum naphtha
- 
- 100 gal. Yield

Viscosity—25 seconds at 70° F., using No. 4 Ford cup

Total solids—27.00%

## FLAT WOOD LACQUER

(Low-Viscosity Type)

- 57 lb.  $\frac{1}{2}$  second nitrocellulose wet with 35% ethyl alcohol  
 81 lb. Maleic resin  
 38 lb. Dibutyl phthalate  
 19 gal. Ethyl acetate  
 13 gal. Butyl acetate  
 7 gal. Butyl alcohol  
 18 gal. Toluol  
 18 gal. Petroleum naphtha  
 38 lb. Aluminum stearate lacquer paste A  
 26 lb. Celite lacquer paste B
- 
- 100 gal. Yield

Viscosity—25 seconds at 70° F., using No. 4 Ford cup

Total solids—27.00%

## LACQUER—NITROCELLULOSE

## ALUMINUM STEARATE PASTE A

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16% by wt.	Aluminum stearate
7% by wt.	5-6 second cotton dry
3% by wt.	Dibutyl phthalate
30% by wt.	Ethyl acetate
40% by wt.	Ethyl alcohol
4% by wt.	Butyl alcohol

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100% by wt.

## CELITE LACQUER PASTE B

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25% by wt.	Celite
12% by wt.	½ second cotton dry
4% by wt.	Butyl acetate
16% by wt.	Ethyl acetate
4% by wt.	Butyl alcohol
4% by wt.	Ethyl alcohol
35% by wt.	Toluol

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100% by wt.

## FLAT WOOD LACQUER

(High-Viscosity Type)

---

24 lb.	5-7 second nitrocellulose wet with 35% ethyl alcohol
132 lb.	Maleic resin
24 lb.	Dibutyl phthalate
20 gal.	Ethyl acetate
14 gal.	Butyl acetate
8 gal.	Butyl alcohol
16 gal.	Toluol
16 gal.	Petroleum naphtha
47 lb.	Aluminum stearate lacquer paste A
31 lb.	Celite lacquer paste C

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100 gal. Yield

Viscosity—25 seconds at 70° F., using No. 4 Ford cup  
 Total solids—26.00%

## CELITE LACQUER PASTE C

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25% by wt.	Celite
8% by wt.	5 second dry cotton
8% by wt.	Butyl acetate
16% by wt.	Ethyl acetate
4% by wt.	Butyl alcohol
4% by wt.	Ethyl alcohol
35% by wt.	Toluol

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100% by wt.

the durability of the finishing system used on their products. This cold check test, which gives a close approximation of the life and durability of the finish, may be compared to the accelerated weathering tests used on paints and enamels. Several factors affect the final results; the type of veneer, the bonding agent, and the time used in preparing and aging of the panel. The following specifications are used at the present time in carrying out the test.

Cabinet veneer panels are finished in the customary manner, using paste filler, sanding sealer, and finishing lacquer. The ends and backs of the panels are sealed to prevent the absorption of moisture. The panels are then permitted to age at room temperature for three weeks to allow all the solvent to evaporate and the films to age properly. The cold check test is carried out at temperatures of 120° F. and -5° F. The panels are first placed in the heating cabinet and kept there for half an hour at a temperature of  $\pm 120^{\circ}$  F. The panels are removed from the heating cabinet and a period of sixty seconds is allowed to transfer same to the refrigerator cabinet where they are kept at -5° F.  $\pm 1^{\circ}$ . The panels are then removed from the refrigerator and allowed to attain room temperature within a minimum of thirty minutes. They are then examined for checks by the naked eye and with the aid of a magnifying glass or a low-power microscope. One exposure in the heating cabinet and the refrigerator cabinet comprises one cycle. A satisfactory furniture or cabinet lacquer is expected to stand a minimum of twelve cold check cycles.

Two types of cold check failures occur. One is a check across the grain of the wood frequently extending the entire width of the panel. This check shows the fracture of the film and extends completely through the finish. The other type of check occurs with the grain of the wood, most frequently directly over the pores. This shows a fracture of a small area and is caused not so much by the lacquer as by the method used in the preparation of the panel, or the finishing system the panel represents.

The cross check, or true cold check, may be seen in reflected light as a break in the film which may run crosswise or diagonally to the grain of the wood. It is similar in appearance to a crack in plate glass. The localized type of check is readily noticeable to the naked eye as the film is both raised and ruptured over the pores of the wood and usually follows the contours of the pores. It is the accepted opinion that this type of check is due either to moisture or solvent which has been trapped in the pores of the wood.

The equipment used for the cold check test has not been definitely standardized up to the present time. Some laboratories use a standard electric oven for the heating cabinet, and a two-hole ice cream refrigerator for the cold cabinet. Where provision is made for circulation of the air inside the cabinets by use of a fan, a considerable variation in readings occurs when these are compared with ordinary types of heating and cooling cabinets.

In order to obtain accurate duplicate readings, it is necessary to use identical types of veneer wood since variations in the composition of the veneer will greatly affect the final readings. Some of the technical groups working on the problem are considering the use of a standard type manufactured surface such as pressboard or composition board, which will eliminate variables of the panels.

### FORMULAS

#### CLEAR BRASS LACQUER

150 lb.  $\frac{1}{2}$  second nitrocellulose wet with 35% ethyl alcohol  
50 lb. Dibutyl phthalate  
19 gal. Ethyl acetate  
13 gal. Butyl acetate  
13 gal. Butyl alcohol  
31 gal. Toluol  
8 gal. 4 lb. cut refined wax-free shellac in alcohol

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100 gal. Yield

Requires reduction with equal parts of lacquer thinner for spraying  
Total solids—27.00%

#### SILVER LACQUER

45 lb. 30 second silver cotton wet with 35% ethyl alcohol  
7 lb. Dibutyl phthalate  
26 gal. Ethyl acetate  
13 gal. Butyl acetate  
7 gal. Butyl alcohol  
45 gal. Toluol  
3 gal. 4 lb. cut gum elemi in toluol

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100 gal. Yield

Viscosity—45 seconds at 70° F., using No. 4 Ford cup  
Total solids—10.00%

### Clear Metal Lacquers

They are used to protect silver, brass, and other tarnishable metals by applying a thin clear film over the surface. Since most metals so

protected are smooth and non-porous as compared with wood, metal lacquers are of higher viscosity and lower solid content than lacquers formulated for use on wood and other absorbent surfaces. Resins, either synthetic or natural, are added to the nitrocellulose to increase adhesion and body, whereas plasticizers are added to secure the desired flexibility. Metal lacquers must be acid-free, crystal-clear, and free of specks or foreign matter, and solvents used must be water-white in color. The solvents must be selected to deposit a clear, homogeneous film on the metal with no blushing from humidity in the atmosphere or from the resin used in the formulation. Brass lacquers often have a high resin content; in some cases yellow or brown dyes may be added to deepen the color of the brass. Silver lacquers are usually made with little or no resin content, using a special grade of water-white nitrocellulose called silver lacquer cotton with a small amount of camphor or other plasticizer to give adhesion and flexibility.

### Textile Lacquers

Textile lacquers are being used in large volume. Pyroxylin coatings have largely replaced oleoresinous materials in the oiled-silk field. They have also replaced rubberized fabrics to a large extent, owing to the lighter weight and the lack of odor of pyroxylin coatings. The attractive appearance and long-lasting qualities of lacquered fabrics have increased their public acceptance so that they are now found in transparent and semi-transparent shower curtains, umbrellas, window curtains, dress shields, baby pants, waterproof sheeting, kitchen jar covers, table cloths, window shades, and similar materials.

Silk was before World War II the most commonly used fabric, because of its light weight and soft feel, but rayon, cotton, and other materials are also used. Coatings are applied on one side or both sides, according to the requirements of the manufacturer.

For one-side coating, the lacquer, usually of the medium-viscosity type, containing film scrap or nitrocellulose of medium viscosity, is applied by a knifing process, the fabric being drawn under a knife, with the lacquer rolling on the material and passing under the knife edge. The thickness of film is regulated by adjusting the tension on the cloth, also the pressure of the knife edge on the material. From the knife edge the coated fabric passes over rollers through a heated drying tunnel, which prevents blushing and also accelerates the drying.

When both sides of the cloth are coated in one operation the material is immersed in a trough containing the lacquer, and then passed between two squeegee rolls, which are regulated to give the required

thickness of film. A tower drying apparatus of much the same construction as used for oiled silk is used for drying, and the coating is similar in composition to that used for one-side coating.

In some plants a forced air unit heater directs a stream of hot air on the coating to hasten drying, and in others a festooning arrangement in a hot air chamber is used. When film scrap is used for the nitrocellulose in the coating, a lower cost finish is obtained, with good tensile strength and abrasion resistance.

Coatings of this type are usually high in plasticizer, which may be raw or blown castor oil, tricresyl phosphate, dibutyl phthalate, or other chemical plasticizers. When a pigmented finish is applied, the pigments are usually ground to the required degree of fineness in castor oil or chemical plasticizer, mixed in with the nitrocellulose solution, and brought to the proper viscosity for application by addition of mixed lacquer thinner.

A light dusting with finely divided mica is frequently employed to eliminate any tackiness or sticking which might occur when the highly plasticized lacquered fabrics are finally rolled up for shipment to the trade.

These coated fabrics, as well as silk, rayon, and cotton dress goods, are often printed with various-colored textile printing lacquers, and many attractive designs and effects are obtained with these materials. The textile printing lacquers are heavily pigmented and highly plasticized lacquers of heavy body and slow drying characteristics, so that they can be applied by the roller printing process with engraved copper rolls. In some instances, a stencil printing method is used, and in both methods a festooning drying arrangement or heated tunnel dryer is employed to dry the lacquer print.

Cotton duck, canvas, mattress covers, and similar heavy fabrics are often coated with a pyroxylin base composition containing pigments, plasticizers, and flame-retarding materials such as barytes, silicates, carbonates, or phosphates to produce a waterproof and fireproof material. The phosphate plasticizers, as tricresyl and triphenyl phosphate, and chlorinated diphenyl (Aroclor) resins are advantageous in flameproofing compositions for this purpose.

### Paper Lacquers

These are used to provide a waterproof, greaseproof, and glossy or semi-gloss finish on paper or cardboard, such as used on magazine covers, advertising folders, and leaflets, catalogs, display signs, and posters, playing cards, wallpaper, and countless other products. Vary-

ing requirements of durability, waterproofness, resistance to discoloration, grease and oil and other service conditions determine the type of formulation to be used.

Paper, because of its high porosity, seems to be a good field for the use of lacquer emulsions, with their advantage of decreased penetration as compared with lacquers made with straight solvents. The usual types of plasticizers are generally used, except where the paper is to come in close contact with food products, when odorless and non-toxic plasticizers, such as the citrates, methyl phthalyl ethyl glycolate (Santicizer M17), and others, are used.

### Gasket Lacquers

These lacquers, clear or pigmented, are applied on the article being coated by means of a gasket, which may be rubber, felt, composition, or metal.

Clear or colored lacquers, of heavy consistency, are applied on pencils by means of a machine which pushes the pencil through a small receptacle in which the lacquer is contained, the gaskets at the exit of the container being specially designed to wipe off the excess lacquer coating, so that the required thickness of film is obtained. Usually four or more coats are applied to give a finish of satisfactory depth and appearance. Since the wooden pencils are impregnated with paraffin wax to give proper sharpening qualities to the wood, it is necessary to formulate pencil lacquers so that the solvents and plasticizers will have little or no lifting or dissolving effect on the wax. Rapid production schedules necessitate fastest drying types of lacquers, so that little or no medium- or high-boiling solvents are used.

Broom handle lacquers are applied by machine or hand dipping. The handle is immersed in a tank containing the lacquer, then rapidly pushed or pulled through a rubber or composition gasket, so that a thin film of lacquer remains on the surface. One or more coats are applied, as required. High viscosity lacquers with high gum content are generally used.

Cable lacquers are used in finishing high- and low-tension ignition cable for automotive, airplane, and other electrical requirements. High-tension cable lacquers are required to meet rigid specification tests, such as flexibility during and after exposure at extremely low temperatures, flexibility after exposure to high dry heat, and after immersion over an extended period in hot lubricating oil. Such lacquers must contain a carefully balanced combination of nitrocellulose



or ethylcellulose,\* along with plasticizers and resins which will meet the requirements of the specifications. Low-tension cable lacquers are not subject to such rigid specifications, and usually contain film scrap, plasticizers, and solvents. Cable lacquers are applied on the cotton- or other fabric-covered cable by passing through a container holding the lacquer. A rubber, felt, or composition gasket, or metal die, is used to wipe off the excess material. Usually a drying tower is used, and multiple coats are applied to get the proper thickness of film. The composition of the lacquer coating is designed so that proper drying is provided in the time allowed between coats and that the finished cable does not stick in the reels when rolled up for shipment.

### Leather Dopes

The leather industry is one of the oldest users of nitrocellulose finishes, and many types of finishes and effects are secured. Nitrocellulose finishes are used to bring out and enhance the natural appearance and feel of fine leathers, to fill the grain, to hide blemishes, and to color and to waterproof the skin.

Since there are vast numbers of tanning methods and wide varieties of hides and skins, a great many different types of lacquer coatings are used to secure finishes as desired by each individual manufacturer. Finishes are applied by brushing, knifing, swabbing, and spraying. In general, lacquers of high oil and plasticizer content are used, with little or no gum or resin content. Both pigmented and clear finishes are applied, some manufacturers preferring to mix their own, using a cotton or film scrap solution as the basic material and adding pigment bases, plasticizers, oils, and thinners as required. Split leathers are built up to a satisfactory appearance with multiple coats of flexible leather lacquers, and patent leathers of good durability are also made by use of combinations of treated linseed, soybean, and other oils with nitrocellulose solutions of cotton or film scrap.

Artificial leather is one of the important materials in production of which large volumes of nitrocellulose materials are used (9). Because of low cost requirements, large amounts of film scrap are used, as well as nitrocellulose of medium viscosity. A good grade of cloth is used for the base, and a number of coats of lacquer are applied to build up a finish which must have good adhesion or solid anchorage, durability, flexibility, toughness, and waterproofness. Application is by knifing, with the cloth under tension passing under a knife edge which applies

\* See Chapter 29, Volume I.

the proper thickness of film, and the dope or lacquer rolling up in front of the knife on the top surface of the cloth. After leaving the knife, the cloth passes through a heated drying tunnel, which may or may not be equipped with a solvent recovery system. Each coat bites into or softens the previous coat, so that one continuous film is formed. The amount of solvent is carefully regulated in each coat, so that no blistering or blemishes occur, which would be the case if too strong a solvent combination were used; or lack of tensile strength, loss of adhesion, or other faults in case too lean a mixture were employed.

Imitation grain and antique leathers are made by coating the cloth in the basic color, engraving under pressure rolls, then rubbing over the fabric with a mixture of solvents and pigments in the desired contrasting shade, which collects in the channels or recesses of the grain, thus producing the antique effect. A weak solvent mixture is used, so that the wiping color will not cut into the basic color too quickly; otherwise a blemished, smeary job results.

### Airplane Dopes

Airplane dopes are solutions of nitrocellulose or cellulose acetate or mixed esters,\* which are applied to the linen or cotton fabric on wings and fuselages of planes to give tautness, tensile strength, smoothness, waterproofness, and resistance to oil and grease. Coating compositions having a low rate of burning are highly desirable, but they must also possess the other necessary features of tautness, tensile strength, and water resistance. Nitrocellulose dopes have superior tautening qualities, greater waterproofness, and lower cost than cellulose acetate, but they have the disadvantage of high flammability. When non-flammable dopes are required, cellulose acetate or cellulose acetate-butyrate compositions should be used. (See Chapters 19 and 20.)

The tautening of the fabric on the frame of the wing is due to the shrinkage of cellulose films on drying. Greater or less shrinkage is accomplished by varying the amount of oil and plasticizer in the formula. Both clear and pigmented dopes are used, with the clear dopes giving greater tautening effect.

Penetration of the first and second coats into the fibers of the fabric is important to secure maximum adhesion, so that first coats are usually thinned more than the top coats. Brush application also assists in penetration and adhesion. Finishing coats are either brushed or

\* See Chapter 20, Volume III.

sprayed, according to the available equipment. In some finishing systems two or three coats of clear dope are first applied, followed by several coats of pigmented dope. Another system uses four or more coats of a semi-pigmented dope, which contains sufficient pigment to protect the clear cellulose nitrate from the actinic rays of the sun and also to impart the desired color to the fabric.

A typical airplane dope formula is given in U. S. Navy Aeronautical Specification D-15d, as follows:

Cellulose nitrate (wet) .....	9.7% by wt.
Glycol sebacate .....	1.5
Ethyl acetate .....	26.2
Butyl acetate .....	19.6
Butyl alcohol .....	6.6
Aromatic petroleum naphtha ....	36.4

Solids content not less than 7.5% by weight.

A somewhat heavier dope is made on U. S. Navy Aeronautical Specification D-12g, by this formula:

Cellulose nitrate (wet) .....	18.0% by wt.
Glycol sebacate .....	2.4
Ethyl acetate .....	19.3
Butyl acetate .....	19.3
Butyl alcohol .....	7.6
Aromatic petroleum naphtha ....	33.4

Solids content not less than 14.0% by weight.

Acidity of both these dopes shall not exceed 0.06 per cent as acetic acid.

A typical cellulose acetate clear dope is given in U. S. Navy Aeronautical Specification D-23a as follows:

Cellulose acetate .....	9.0% by wt.
Tricresyl phosphate .....	1.0
Ethyl lactate .....	14.0
Ethyl acetate .....	14.0
Methyl ethyl ketone .....	31.0
Acetone (Grade A) .....	31.0

Solids content shall be not less than 10.0% by weight.

In the above formulations, nitrocellulose of the medium viscosity type (20 to 30 second) is generally used; in the acetate dopes, special types and grades of cellulose acetate are required.

Aluminum dopes are made by adding aluminum paste or powder to a small amount of proper thinner, then adding to the clear dope. They are applied in the usual manner.

## Nail Polishes

Nail polishes are solutions of nitrocellulose in mixtures of esters or ketones and alcohols, with little or no hydrocarbons. Various tints are obtained by addition of red or maroon pigments and dyes to titanium dioxide or other white pigments. Small amounts of resin and plasticizer are also added, to give satisfactory adhesion and luster.

## Lacquer Cements

Cements are used in large volume in the shoe manufacturing industry and are applied both by machine and by hand (5). Various other manufacturers of leather, fabric, and composition specialties utilize the quick drying and toughness of lacquer cements in the fabrication of their products.

These are used for a multitude of general applications, and are also put up in small collapsible tubes for household use.

They are waterproof and durable, with especially good results being obtained on porous surfaces, such as leather, fabrics, wood, and composition materials. A thin coat should be applied first to both surfaces and allowed to dry so as to secure penetration. Then a heavier coat is applied, and both parts pressed firmly together. Drying takes place in a short time, resulting in a firm, tough, waterproof joint.

Such cements vary with the application requirements. They are usually made up of film scrap, celluloid scrap, or medium viscosity nitrocellulose (15 to 20 second) dissolved in a solvent blend of fast-evaporating solvents, such as acetone, ethyl acetate, alcohol, and benzol or toluol. Small amounts of gum or resin and plasticizer or oils are sometimes added (5).

A typical formula for general purpose cement is:

Film scrap .....	10.0% by wt.
Castor oil .....	2.0
Acetone .....	10.0
Ethyl acetate .....	20.0
Butyl acetate .....	5.0
Denatured alcohol .....	20.0
Benzol (90 degree) .....	30.0
Tricresyl phosphate .....	2.0
Ester gum .....	1.0

## Plastic Wood

Plastic wood is made by wetting wood flour, or finely ground wood pulp, with a small amount of solvent, such as ethyl acetate, and mixing this paste with a lacquer cement. A suitable material would con-

tain approximately 20 per cent wood flour and 80 per cent cement. This can be used to fill nail or worm holes, cracks, etc. It dries rapidly, after which it can be cut or machined, very much like the wood itself.

### **Pigmented Lacquer Enamels**

**Automotive.** Lacquer enamels of the automotive type are among the best and most durable exterior finishes on the market today. They are used for finishing all types of automobiles, trucks, buses, and also railway equipment and other equipment or articles which are subject to the most extreme conditions of exterior exposure. They must be waterproof, not affected by weather or sunlight, or the fluctuations of temperature and atmospheric conditions found in all parts of the world, from the tropics to the subarctic regions. Pigments used must be the most permanent and non-fading type. They must be ground to extra fineness to secure the full beauty and tone of the colors, and also to enable rubbing to a high degree of smoothness and luster. Pigment content is usually kept to the minimum degree that will permit satisfactory coverage and protection. The pigments also add to the durability of the finish by decreasing the penetration of actinic rays of sunlight into the body of the film. Increased durability and adhesion are controlled by proper selection of the resins and plasticizers. Of these, the alkyd resins, dammar, and ester gum are most widely used, along with dibutyl phthalate, tricresyl phosphate, and raw or blown castor oil as plasticizers. The ratio of resin to nitrocellulose is usually low when natural resins are used, but with the more durable alkyds the ratio is as high as 2 or 3 parts resin to 1 part nitrocellulose, the exact amount varying with the pigments and degree of luster desired. The plasticizer content is also dependent on the amount and type of pigment, as well as the amount and type of resin in the formula, and the flexibility requirements of the finish.

**Industrial Lacquer Enamels.** These may be of either exterior or interior type. They are used for finishing such articles as refrigerators, metal furniture and equipment, wooden furniture, electrical apparatus, clocks, toys, and novelties. Composition depends in general on service requirements, durability, and other factors, but ordinarily resin to cotton ratios are higher than in automotive enamels, also pigment concentrations are higher.

**Crackle Enamels.** These are heavily overpigmented lacquers containing a minimum of cotton and resin binder. When they are applied over a colored lacquer undercoat, they shrink or contract to form

islands and show the ground color in the form of fine irregular lines or veins. A finishing coat of clear gloss or flat lacquer is necessary to protect the crackle lacquer and prevent the pigment from being rubbed off when handled.

**Crystal Lacquers.** These are either clear or colored lacquers which contain some crystal-forming substance as naphthalene or phthalic anhydride, together with specially selected medium- and high-boiling solvents, such as methyl-cyclo-hexanol or tetralin. They are sprayed on metal, glass, or other non-porous surfaces. When allowed to dry in a room free from drafts at temperatures of 65 to 75° F., a finish of intricate crystalline design results. The size and shape of the crystals is controlled by the ingredients as well as the method of application and drying conditions. Patterns vary from small needlelike crystals to large peacock feather effects.

**Primers.** Primers for metal are usually of the oleoresinous air-dry or baking type, pigmented largely with iron oxide or zinc chromate pigments, with the necessary inerts to give desired adhesion and filling qualities. Synthetic air-dry and baking primers are also used where faster production schedules are required. For maximum fast air drying, lacquer primers are used.

#### GRAY LACQUER PRIMER

Grind in pebble mill.

144 lb.	Titanium dioxide
8	Zinc oxide
88	½ second nitrocellulose wet
25	C. D. alcohol
43	Ethyl acetate
43	Amyl acetate
50	Toluol
3	Lampblack
404 lb.	Total yield

Mix 240 pounds of the above grind in a mixer with the following:

70 lb.	½ second nitrocellulose wet
20	C. D. alcohol
125	Ethyl acetate
125	Amyl acetate
40	Toluol
130	8-pound cut dammar solution
44	Dibutyl phthalate
88	Pale blown castor oil
882 lb.	Total yield

**Surfacers.** Surfacers for metal are made up of oleoresinous, synthetic, or lacquer base materials, and contain a high pigment content to give filling and smooth sanding characteristics.

#### GRAY LACQUER SANDING SURFACER

Grind in pebble mill.

170 lb.	Zinc oxide
170	China clay
3	Lampblack
70	Modified maleic resin
40	½ second nitrocellulose wet
20	C. D. alcohol
30	Ethyl acetate
48	Amyl acetate
158	Toluol

---

709 lb. Total yield

Mix 500 pounds of the above grind in heavy-duty mixer with the following:

62 lb.	½ second nitrocellulose wet
25	C. D. alcohol
45	Ethyl acetate
45	Toluol
25	Dibutyl phthalate
25	Amyl acetate

727 lb. Total yield

**Putties.** Glazing putties are also made up on either an oleoresinous, synthetic, or lacquer type of formulation. They are highly pigmented and contain a low volatile ratio to solid-forming ingredients, to allow maximum filling, together with adhesion and sanding qualities.

#### GRAY LACQUER SPOT PUTTY

Grind in pebble mill.

90 lb.	Zinc oxide
90	China clay
36	Modified maleic resin
32	Toluol
12	Dibutyl phthalate
1.5	Lampblack
9	Butyl propionate

---

270.5 lb. Total yield

Mix the above grind with the following paste in a dough kneader:

70	lb.	$\frac{1}{2}$ second nitrocellulose wet
22		Amyl acetate
92	lb.	Yield
362.5	lb.	Total yield

As no finish is any stronger than its foundation or undercoats, it is extremely important that suitable primers, surfacers, and glazing putties be used in the lacquer-finishing system. Since lacquer enamels have a tendency to dry with uniform thickness of film all over the coated surface, any rough spots, pits in the metal, file marks, and other imperfections must be filled in and sanded smooth in the undercoats; otherwise the lacquer enamel finish would magnify any rough spots. Undercoats, particularly those of oleoresinous and synthetic base, must be especially formulated to be impervious to the lifting or wrinkling action of lacquer thinners when lacquer enamel topcoats are applied, and thorough testing of this is advisable before use of undercoats on a production schedule. Lacquer primers and undercoats are not usually troublesome in this respect, although any oxidizing type of oil or synthetic resin, if used in large amount in lacquer type undercoats, may be susceptible to lifting after a certain drying period. Use of such materials in small amounts or eliminating them entirely is safer practice. Typical formulas of lacquer primer, sanding surfacer, and spot putty are shown on pages 551 and 552.

#### FACTORY LAYOUT FOR THE MANUFACTURE OF LACQUERS

In consideration of the highly inflammable nature of the materials used in the manufacture of lacquers, it is recommended that the manufacturing building be separate and located at some distance from other factories or residences. A railroad siding is very helpful, since it enables the manufacturer of lacquers to purchase his solvents in tank cars, providing for greater economy.

The volume of production planned will largely determine the type of plant to be designed. A lacquer factory may be a very simple and inexpensive layout requiring only several mixers, or a very elaborate affair including storage tanks, metered pipe lines for solvents, various types of pebble mills and roller mills, and a large assortment of mixers, cutters, filter presses, and centrifugal clarifiers. A simple layout may operate efficiently because numerous steps in the manufacture may be saved by purchasing partly fabricated materials. Nitrocellulose need not be purchased in dry form, since cotton solutions of various types



may be purchased and delivered to the lacquer manufacturer in drums. Pigment pastes may be purchased ground in any vehicles desired. This eliminates the installation of expensive mills. Solvents and diluents may be purchased in tank wagons or steel drums, thus eliminating storage tanks.

For large volume production, it is desirable to have six or more 6,000-gallon storage tanks adjoining the manufacturing building. Pipe lines running from these tanks lead to a weighing tank located near the ceiling of the main mixing room or through a meter, so that, after the required amounts are pumped out from each tank, the solvents may run by gravity into the cutting or mixing tanks.

A properly equipped laboratory should adjoin the plant, so that the various products manufactured may be tested before they are run out of the mixers. Technical control is essential in the production of lacquers, and a competent chemist should be in charge of the factory and laboratory at all times.

Safety measures in the lacquer factory cannot be overemphasized. The fire-fighting equipment and sprinklers should be inspected frequently. It is essential to guard against static electricity, and all tanks, belts, pulleys, motors, etc., should be properly grounded. No matches should be permitted in the factory, and all tools should be made of bronze to prevent sparks.

### Cutting of Cotton

One of the most important steps in the manufacture of nitrocellulose lacquers is the dissolving or "cutting" of the cotton. Most cotton solutions are made with the nitrocellulose concentration as high as possible, the exact percentage of cotton in the solution depending on the viscosity of the cotton and the solvent combinations used. Formulas are usually made up to take an even number of barrels of nitrocellulose, since the wetting alcohol may be present in greater amount in the cotton at the bottom of the barrel than at the top, and errors in formula and mixing are thus minimized.

Where non-solvents, such as coal tar distillates, benzol, toluol, xylol, or petroleum fractions, enter into the formula, they are generally put into the mixer first. Then the cotton is added, with agitation. After the non-solvent has wet the mass of cotton, the active solvents such as ethyl acetate and butyl acetate are added, and agitation is continued until the solution is clear and free from lumps. When the cotton is cut in a solvent mixture, without any diluent or non-solvent, there is a tendency for it to ball up into lumps of varying sizes, with

the outer portion gelatinized by the solvent and the inner layers dry and undissolved. Such solutions require a heavy-type mixer with good agitation to break up the lumps and secure complete solution.

This may be accomplished in various type agitator mixers, and, since the solvents are volatile, the apparatus should be air-tight. It should have a large manhole equipped with suitable gasket and cover, and also a large gate valve for drawing off the finished solution.

Although steel is the metal commonly used in construction of agitator tanks, it has some discoloring effect on the cotton solution, so that, for maximum paleness of color, aluminum, tin, or white metal tanks are employed. For silver lacquers, which are required to be water-white, glass-lined tanks are most satisfactory. Shafting and agitator blades may be made of Monel metal, aluminum, or other non-corrosive material. Revolving churns, or wooden barrels equipped with baffles, are used in smaller plants.

Kneading and mixing machines of the Baker Perkins or Werner Pfleiderer type are used to produce extremely heavy and viscous solutions, the agitator blades revolving in opposite directions, but meeting at close clearance at each revolution, which provides thorough agitation and breaking up of lumps.

The Turbo Mixer, one of the newest mixers for cotton cutting, consists of a large cylindrical tank with a turbo rotary agitator at the bottom of the rounded base tank. The rotary agitator is surrounded with deflector blades, which direct the solution upward and around the sides of the tank, from which point the solution goes down into the center and again to the bottom and through the agitator blades. This machine is very satisfactory for solutions of medium to low viscosity.

In all cotton-cutting machinery, it is important to allow sufficient clearance between agitator blades and side walls or bottom of the tank, so that lumps or balls of undissolved material are not subjected to a high compression or friction, which might easily result in a fire or explosion in the apparatus. The machine should also be well-grounded and belts or shafting freed from accumulations of static electricity with suitable metal dischargers and ground wires. Good housekeeping around the cutting apparatus is also essential, as any accumulation of dry nitrocellulose dust or particles of film scrap are highly inflammable and need only the slightest spark to start a fire.

Many lacquer manufacturers do not cut their own cotton but buy it in solution form, in a specified solvent mixture. Such solutions are available in all the common viscosities, and are supplied in tin-lined

or galvanized open head drums, in concentrations of 10 to 35 per cent solids, depending upon the viscosity of the cotton. The lacquer manufacturer is thus saved the fire hazard and expense of making and clarifying his own solutions, and subsequently he has lower investment in plant and inventory.

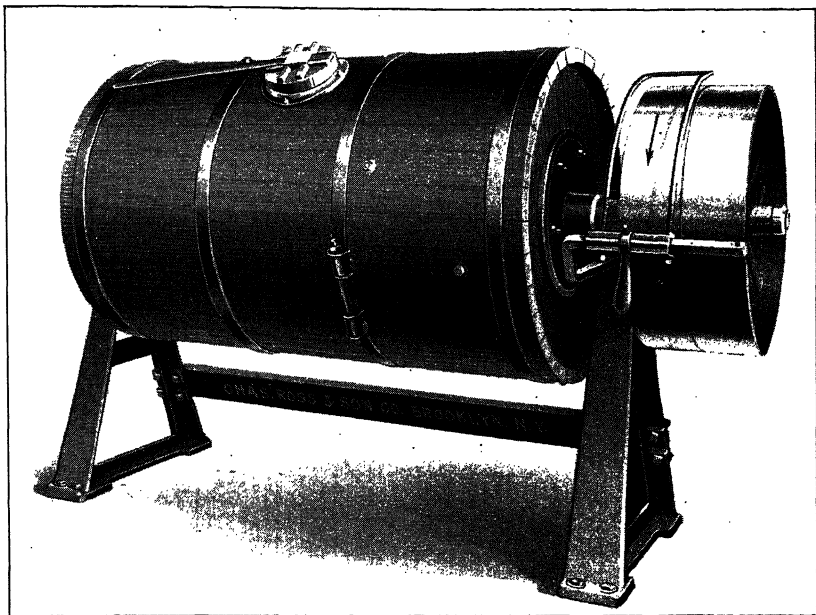
As nitrocellulose lacquers are colloidal solutions and cotton solutions are of gel structure, they are subject to the physical variations typical of these solutions. Heat decreases while cold increases viscosity of nitrocellulose solutions. These solutions do not reach their true viscosity immediately after they are made. Observation has shown that the true viscosity is reached after the solution has been made up for four or five days, providing the temperature has remained constant during that time. Certain solvents produce solutions of lower viscosity than others. This has already been discussed in the section on solvents. It should be mentioned that addition of a non-solvent such as toluol will at first cause a decrease in viscosity; then further addition will cause flocculation and precipitation of the nitrocellulose in jelly form. Therefore only a limited amount of toluol or other non-solvent can be used.

### Cutting of Resin

In lacquer manufacturing, the resins used are those which are soluble in coal tar distillates, such as benzol, toluol, and xylol, or mixtures of these solvents with petroleum naphthas, alcohol, or ester solvents, as ethyl, butyl, and amyl acetate. The resins are usually dissolved cold, in a slowly revolving churn or barrel, such as used for shellac, or an agitator tank with a tight cover to prevent solvent losses by evaporation. Wooden or metal tanks are commonly used. Dammar gum solutions are usually dewaxed as previously described.

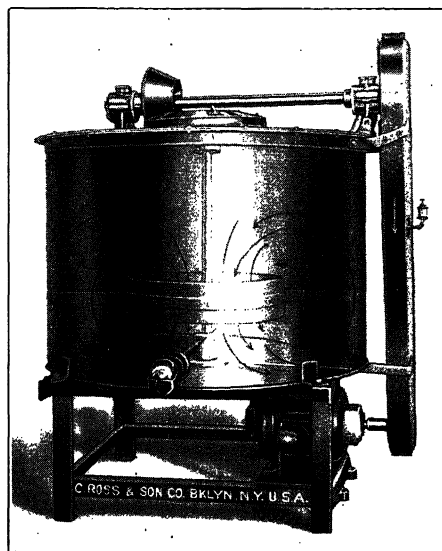
After the gums or resins are in solution, which may require four to eight hours or more, the solution is filtered, centrifuged, or run into storage tanks to be clarified by settling. Clarification by filtration is somewhat difficult and tedious, owing to the gelatinous and slimy condition of the residues and impurities; clarification by centrifuging is the quickest and most convenient method. Several types of centrifuges are in common use, such as the Sharples, DeLaval, and Lacta.

In the Sharples machine, the particles collect on the sides of the rapidly spinning bowl, which may be varied in speed from 6,000 to 17,000 r.p.m. (revolutions per minute). The centrifugal or clarifying force increases with the speed of the machine. Its effect may be controlled by the rate of feed of the solution, slow feed allowing the



*Courtesy of Chas. Ross & Son Co.*

FIG. 10. Revolving Churn.

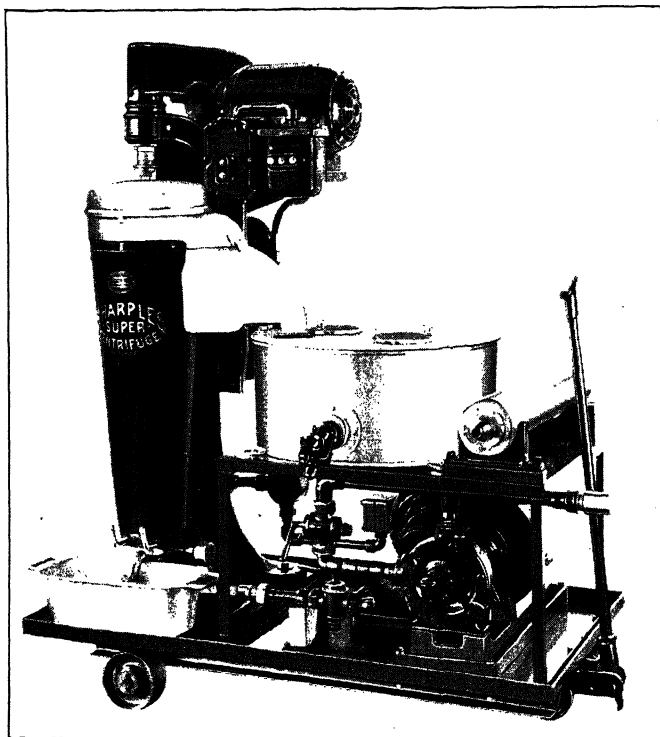


*Courtesy of Chas. Ross & Son Co.*

FIG. 11. Vertical Gum-Cutting Tank.

solution to remain longer in the bowl, with greater clarification resulting.

The DeLaval centrifuge is of different construction, but operates on the same general principle. The original material is run in at the top of the rapidly revolving bowl and passes through a series of in-

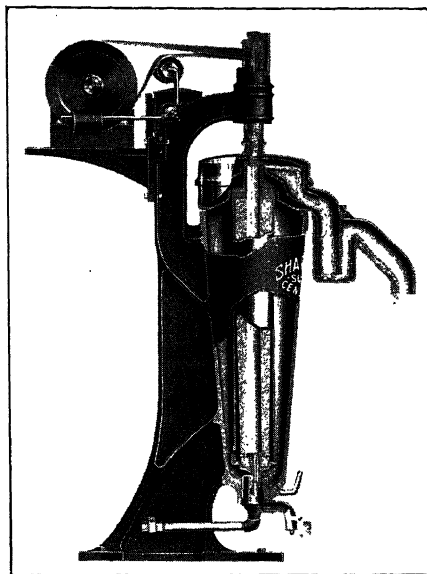


*Courtesy of Sharples Chemicals Co.*

FIG. 12. Sharple's Super-Centrifuge.

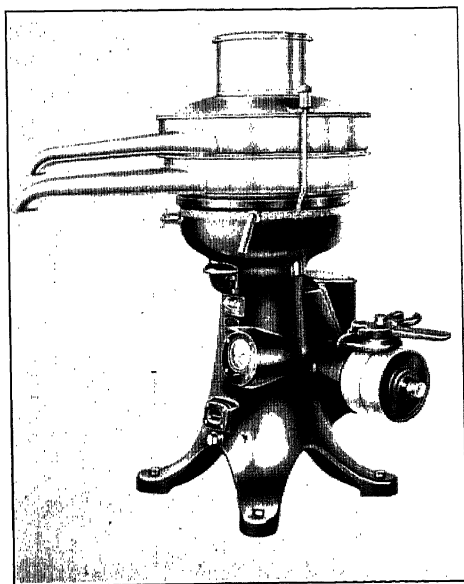
verted cone filter plates, where it is acted upon by the centrifugal force. The undissolved solid matter is caught on the disks between which the liquid passes, and thrown to the sides in the form of a cake. When colored enamels are run through, the gears must be adjusted so that only the required amount of pigment particles is removed. The plates are somewhat more difficult to clean than the bowl of the Sharples machine.

The Lacta clarifier is simple, economical, and easy to operate. The liquid enters the top, is carried to the bottom of the bowl, where it



*Courtesy of Sharples Chemicals Co.*

FIG. 13. Sharples Super-Centrifuge (detail).



*Courtesy of Lacta Separator Company, Inc.*

FIG. 14. Clarifying Separator.

receives in the lower clarification chamber its first step in cleaning, with removal of the heavy particles. The second degree of clarification takes place on the inner side of the top plate, and the third degree of clarification occurs on passage of the liquid around the outer side of the top plate. It is thus possible to make the fine adjustments which are necessary when clarifying pigmented lacquers with this machine.

All centrifuges are required to be equipped with explosion-proof electric motors, and it is also desirable that they have the vapor seal fittings which are recommended for lacquer work.

For further data on centrifuges, see Chapter 24.

Some manufacturers do not centrifuge their gum solutions but merely strain them through several layers of cheesecloth, factory cotton, or other filtering medium to remove the large and undissolved particles. Then they run the finished lacquer or enamel through the centrifuge, thus saving an operation; and in many cases this is sufficient for ordinary production requirements.

In some lacquer-manufacturing plants, it has been found that it is unnecessary to make separate gum solutions, thus saving another operation. After the cotton is in solution, the additional solvents, plasticizers, etc., are added; then the solid resin, in the form of lumps or small particles, is added, with constant agitation. Complete solution results in approximately four hours. It is essential that only resins which are completely soluble without formation of residue be used in this manner.

### Grinding of Pigments

Pigments, as used in lacquers, are obtained from the dry color manufacturers in a finely divided state, so that the problem is one of dispersion in vehicles which are desirable in the finished lacquer enamel. Raw or blown castor oil are good grinding media, and are commonly used for pigment dispersions, as are blends with plasticizers such as dibutyl phthalate and tricresyl phosphate. In some instances where the oil and plasticizer contents of a material are low, it is necessary to add gum solution, such as ester or dammar, to the grinding vehicle; this has the effect of increasing the luster of the finished enamel. Several types of mills are in general use, each having its advantages.

**Pebble and Ball Mills.** These depend for their grinding action upon the impact and crushing, and also polishing effect of a large number of pebbles or steel balls contained in a revolving drum. In the pebble

mills, the mill is lined with specially selected stone, and the mill is filled about one-half full of smooth rounded pebbles of proper size.

Pebble mills are generally used for grinding flat whites, tints, primers, surfacers, and other heavily pigmented lacquers. A certain amount of skill or technique is necessary to get best results with pebble mills; and this must be determined from experience for each specific formula. It is essential to have pebbles of suitable size, proper viscosity of the batch to be ground, and correct speed of the mill. A certain amount of air space should be left in the mill, as overcharging results in improper grinding. The noise of the pebbles should be faintly audible when the mill is rotating. Viscosity of the batch can be adjusted as required by addition of thinner or high-viscosity cotton solution. The time required for satisfactory grinding is usually twenty hours or longer; small samples for testing purposes can be drawn off at desired time intervals. Once the mill has been charged and the formula standardized for viscosity, the principal advantages of the pebble mill are that it is entirely enclosed, so that evaporation losses are cut down to a minimum and little attention is necessary during the grinding.

Ball mills are similar in operation to pebble mills, except that they are filled with small steel balls and are equipped with a smooth steel lining and with a water-cooling jacket when desired. They are best used for grinding black and dark-colored pigments. The steel ball mill requires less time for pigment dispersion than the pebble mill, and it produces enamels which have higher gloss.

**Roller Mills.** Three-roller mills and five-roller mills are commonly used for grinding pigmented pastes as used in making colored lacquer enamels. The grinding medium is generally castor oil, or other oils, plasticizers, such as dibutyl phthalate, trieresyl phosphate, or combinations of these with gum solutions cut in xylol, high-flash naphtha, or other slowly evaporating solvents. The pigment and grinding media are mixed to a paste in the usual type of paint paste mixer, and then put on the rolls. The amount of vehicle varies with each pigment. It may average 20 to 30 pounds per 100 pounds of pigment, with higher amounts of liquid being required by such pigments as carbon black and prussian blue. With three-roller mills, several runs over the rolls are usually necessary to secure the required fineness of dispersion for smooth, glossy lacquer enamels; with five-roller mills, however, one pass is sufficient, except with pigments which are difficult to wet or grind.



**Stone mills**, mounted singly or in tandem, are also used for grinding lacquer pigment pastes, with similar procedures as used in paint and enamel grinding. These mills give very fine glossy pastes, but, having low speed of production and requiring constant supervision, they are expensive to operate. Evaporation losses are high on mills of this type. For further data on mills and grinding equipment, see Chapter 24.

### Mixing and Tinting

The mixing and tinting operations are preferably carried out in totally enclosed agitator tanks, many types of which are in common use. Change can mixers equipped with agitator blades which can be raised to permit removal of the holder for filling of the enamel into packages are useful for small and medium-sized batches. Agitator blades which are adjustable and easily removable for cleaning are almost essential with this type of equipment.

Stationary agitator tank mixers are used for large batches of one hundred gallons or more. They are equipped with air-tight covers and a manhole opening for charging and cleaning. Provision should also be made for some automatic fire extinguishing apparatus, such as Foamite, carbon dioxide, or similar material on all lacquer-mixing and tinting equipment.

**Straining** of lacquer enamels is a necessary procedure as there are always some undissolved particles as well as oversize and incompletely ground pigment or foreign matter present. Best results and fast production are obtained by running the pigmented lacquer enamel through a centrifuge. This should be equipped with vaporproof motor and vapor seal. These centrifuges are similar in operation and description to those outlined under gum solution clarifying. More careful control of the feed is necessary with pigmented enamels so that just the proper amount (not too much) of pigment is removed from the enamel. Proper adjustments of the machine for each color are best determined by experience.

With small batches, and where centrifuges are not available, straining is accomplished by filtering through several thicknesses of cheesecloth, factory cotton, wire screen, or other suitable filtering media. It can be stretched over the top of a round container that is equipped with a spigot at the bottom, through which the filtered material is drawn off into packages for shipment.

## Storage

Solvents are best stored in underground tanks, equipped with gages to indicate the level and volume of each solvent. A pump is used to draw solvent from the storage tank for mixing purposes, and the quantity of solvent used is measured by running the solvent through a recording meter. Solvents not purchased in tank car quantities are usually stored in drums and measured in desired amount by weight or volume as used.

Nitrocellulose and film scrap are preferably stored in a building separate and remote from the manufacturing building, and only such quantity as required for the day's production is brought into the mixing room. It is also desirable that the cotton-dissolving tank be in a separate building and remote from the tinting, mixing and filling departments, as a safety precaution.

Cleanliness and good housekeeping are essential around a lacquer plant, as carelessness may result in a disastrous fire, with serious damage to property and possible loss of life. No matches should be allowed on the person of any workman or visitor in the plant, and all machinery, belts, shafting, and equipment should be provided with adequate ground wires to eliminate any static electricity, which might cause sparks. Tools should be made of bronze or other non-sparking metal. Fire extinguishers should be placed at convenient spots around the plant. Safety exits should be provided for all workmen, so that in case of fire in any part of the building no workman would be trapped without exit.

## Application Methods and Equipment

The methods of application used with nitrocellulose lacquers may be classified as follows:

- |              |              |
|--------------|--------------|
| 1. Spraying. | 4. Coating.  |
| 2. Dipping.  | 5. Brushing. |
| 3. Tumbling. | 6. Whirling. |

These listings are in order of commercial importance.

**Spraying.** This is the most commonly used method of application, and is suitable for manufactured articles having a large surface area, so that the size and shape of the coated surface can be efficiently and economically sprayed. The lacquer, which may be clear or pigmented, is reduced to the proper spraying consistency and placed in an enclosed container, which is equipped with air-tight gasket and

seal, so that the lacquer can be put under slight pressure to enable free flowing through the feed line leading to the spray gun. Such containers may hold 5 to 50 gallons or more of material, and, if the lacquers are pigmented, should also be equipped with agitators to insure uniform pigmentation and color of the material at all times. The lacquer is forced through a spray nozzle, along with air under pressure, the air having been previously filtered and cleaned from moisture, oil, and other foreign matter. Pressure on the material tank varies with the type of equipment and installation, usually from 5 to 10 pounds being sufficient. Pressure on the air line to the spray gun also depends upon local conditions, and may vary from 50 to 100 pounds. The material container may be held at room temperature or heated, as desired. Recently some results have been secured with application of "hot" lacquers, where the lacquer is heated by means of electrical heaters or steam coils to a temperature of 160 to 190° F. This results in reduced viscosity of the lacquer and enables spraying of a higher solids content, with reduced costs through lower solvent losses. Manufactured articles, such as automobiles, railway coaches, locomotives, refrigerators, radio cabinets, pianos, furniture, electrical equipment, airplanes, trucks, and buses, are usually finished with the spray method. It is desirable that the coated objects be placed in a room free from dust during the drying period, as any dust or foreign particles which may become lodged in the film will cause blemishes which add to the difficulties and increase time required in rubbing and polishing the finish.

**Dipping.** Dipping was one of the earliest methods used in finishing lacquered articles, and is especially suitable for small articles having rounded or cylindrical surfaces, which are adapted to economical finishing in this manner. Such objects as brush handles, toys, wire goods, and materials of similar size and shape are finished by dipping. Numerous machines for automatic dipping have been developed. These generally immerse the article in a tank filled with lacquer. The object is then withdrawn from the lacquer slowly, at the rate of 2 to 6 inches per minute, depending upon the size and shape of the object and the type of coating applied. The rate of withdrawal should be approximately the same as the downward flow of the lacquer, to eliminate runs or drips. Tanks for dipping lacquer should have as little surface as possible open to the atmosphere.

**Gasket Coating.** Lead pencils are coated by a variation of the dipping process known as gasket coating, wherein the pencils are quickly pushed through a container of lacquer and come out through a tight-

fitting gasket of rubber, felt, or composition, which leaves only a thin film of lacquer on the pencil. A number of coats are applied in this same manner to give the required finish. Gasket lacquers are much more viscous in body than spray or dip lacquers.

**Tumbling.** Small wooden objects, such as handles, golf tees, and the like, are often finished by tumbling in a rotating barrel with a heavily pigmented lacquer enamel. The required amount of lacquer enamel is placed in the barrel along with a definite number of wooden pieces to be finished, and, after rotation for a period of time necessary to secure uniform coating, the pieces are removed and placed on a wire screen or other suitable surface for the drying period. A wire cover on the tumbling barrel permits escape of volatile solvent and assists in drying the finish.

**Roller Coating.** Lacquers are often applied to cloth, paper, and metal by the roller coating process, which is accomplished by means of various types of machines. This method is particularly applicable to large flat-surfaced objects. In this method, the lacquer is placed in a trough or tray, in which a composition roller revolves and picks up the lacquer, transferring it directly to the cloth or paper, or by means of a secondary or intermediate roller. With this process, a coating of any desired thickness can be applied in continuous production.

**Knifing Doctor Blade Method.** The knifing process is used in textile and artificial leather finishing and for lacquering paper. In this method, a lacquer of fairly high viscosity flows or rolls on the cloth, which is drawn under a knife edge. The tension on the cloth and the height of the knife from the surface of the cloth are regulated to secure the required thickness of lacquer coating.

**Printing and Stenciling.** Textile printing with lacquer enamels is accomplished with a rotary printing process, using copper engraved rolls and a heavily pigmented lacquer enamel of proper solvent and solids content. Lacquer printing is often accomplished with the stencil method, which also requires a heavily pigmented and plasticized coating.

**Brushing.** Brush application of nitrocellulose enamels and lacquers is not widely used, owing to the tendency of the average person to attempt to brush the material too long. Brushing lacquers can be used only on relatively small surfaces. Improvements in synthetic resins as well as slow-evaporating, high-boiling solvents have enabled lacquer manufacturers to produce brush lacquers of much easier working qualities than formerly, but the public demand for fast-drying enamels has

been met largely with oleosynthetic resin, varnish-type products. Brushing lacquers are generally made up with a high oil and plasticizer content, with high pigmentation, and can be applied with a soft brush by flowing on the material, with just enough brushing to smooth out the enamel to uniform coverage. A certain amount of skill and technique is required, as too much brushing will cause brush marks, lifting of the undercoat, or roughness of the finish. The proper technique can be readily acquired by unprejudiced workmen. When a fast-drying finish of good toughness and durability is required, brush lacquers will be found satisfactory. Since lacquer solvents have a softening effect on rubber, a special brush with the bristles set in glue or other suitable cement should be used, and the brush must be cleaned out with lacquer thinner immediately after using.

**Whirling.** This process is a special development of the dip process, and is particularly suitable for small objects as metal parts, toys, etc. The objects are placed in a wire or perforated metal basket of circular design, dipped in the lacquer, which is usually thin in body, then placed in the whirling machine, where the excess lacquer is removed by centrifugal force when the basket is rotated rapidly. The excess lacquer is caught in the outside container and can be used over again. The whirling also causes partial drying of the lacquer, which is completed by emptying the container and placing the coated articles on a wire screen or other surface for final and hard drying. The operation is fast and economical for coating small objects of the proper size and design for this method.

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## CHAPTER 19

### CELLULOSE ACETATE

MICHAEL A. DORIAN

#### HISTORY

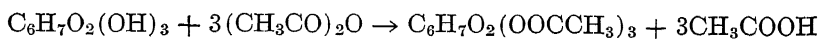
Cellulose acetate is an acetylated carbohydrate which was brought to light by Schutzenberger in the year 1865 (8). Thirty years passed before a process for preparing a cellulose acetate for commercial use was patented (2). A number of patents have been issued since that time dealing with improvements in the process. The first patent for the composition of a lacquer containing cellulose acetate was granted in 1910. These early lacquer products were intended mostly for the impregnation of paper and cloth to impart waterproofness, or to decrease inflammability. Most of these coatings contained cellulose acetate in a solution of acetone, plasticized with available plasticizers (6).

#### MANUFACTURE

The manufacture of cellulosic derivatives involves substitution in the alcoholic OH groups of the cellulose. There are great differences in the reaction conditions, etc., hence also in the production procedure.

Among the cellulosic derivatives, nitrocellulose is unique in that the fiber structure is always retained during conversion. This is not usual with other ester derivatives, since the fibers dissolve during acetylation. The degree of esterification of the commercially useful cellulose esters lies between the diacyl and triacyl stages.

The first step in the manufacture of cellulose acetate is the formation of the triacetate, which is the first chemical reaction product of acetic anhydride and purified cellulose in the presence of suitable catalyst and solvents, such as acetic acid. The reaction may be expressed as follows:



In its most highly esterified form, it has an acetyl content of approximately 44.8 per cent (62.5 per cent as combined acetic acid). The commercially useful grades of cellulose acetate are the result of the carefully controlled hydrolysis of the triacetate. These commercially available hydrolyzed types, which fall within the acetone soluble range, have an acetyl content of 37–42 per cent (51.0–58.6 per cent as combined acetic acid). They are made in various viscosities and all are soluble in a wide range of useful solvents.

The solubility of the cellulose acetate changes continuously with progressive hydrolysis. According to Verner and Engelmann (10) the increase of polar groups in the cellulose acetate calls for a corresponding change in the solvent. Therefore chloroform in admixtures, with small amounts of alcohol, are solvents for the products formed at the highest stage of acetylation; solvent mixtures much richer in alcohol or acetone are solvents for the medium stage product; and acetone-water mixtures are solvents for the lowest stage product.

A study of the comparative permanent stability of cellulose derivatives indicates that ethylcellulose, cellulose acetate, and cellulose acetate butyrate and propionate are superior to nitro- or benzylcellulose.

### GENERAL CHARACTERISTICS

Some cellulose esters do not possess a definite melting point below the decomposition temperature. The addition of plasticizers decreases the melting point, and the decrease is in direct proportion to the amount of plasticizer added. On the other hand, the ether derivatives, for example, ethyl- and benzylcellulose, melt without the addition of plasticizer.

Also, the tensile strength or toughness of the film is higher with the ester derivatives of cellulose. Elongation is the reverse of the tensile strength.

The water resistance of cellulose acetate is in direct relation to the acetyl content, and within certain limits the water absorption is a linear function of the acetyl content. This is also true of the other cellulose derivatives; that is, the water resistance increases with increasing esterification or etherification.

Cellulose acetate has the property of transmitting ultraviolet light, which does not pass through window glass. This, coupled with its toughness, makes it an ideal material for use in hot-bed frames and solariums.

## PROPERTIES

TABLE I

TABLE OF PROPERTIES (5)

*Color—Odor—Taste—None**Melting Point:*

% Acetic acid in ester .....	62	58	56	53	51
Capillary melting point, °C.....	270-290	260-280	240-260	235-245	250-270
Thermoplasticity or molding properties.....	None	Fair	Good	Very Good	Good

*Density:* At 25° C., acetone soluble types = 1.4 (Bulking value = 0.085 gal./lb.)*Refractive Index and Optical Properties:*

Refractive index of films (Abbé) = 1.48  
 Transmits light down to 2,900 A.U. (transmits all solar ultraviolet)  
 Fluoresces slightly in ultraviolet, shows double refraction

*Electrical Properties (Cellulose Acetate Films):*

High internal and surface resistance—60 cycles, 20° C.  
 Dielectric strength, volts/mil = 3,000 (0.0012 inch film)  
 Dielectric constant = 4.2 - 4.8  
 % Power factor loss, 60 cycles = 1.8 - 2.2

*Water Resistance:*

Absorption of moisture by flake material					
% Acetic acid in ester .....	62	58	56	53	51
% Water absorbed, 100% R.H. @ 25° C. (equilibrium) .....	3.5	7.0	8.6	15.1	16
Water permeability					
K = gm./cm. <sup>2</sup> /cm./hr. @ 25° C. ( $\times 10^{-6}$ )...	4.0	4.5	5.0	7.0	..

*Chemical Resistance:*

Resists heat, weak acids, oils, greases, and fats. Not resistant to alkalis except in high acetylations.  
 Lower acetylations (51.57%) soluble in acetone and lower ester solvents, materials above 60% soluble chiefly in mixtures of chlorinated solvents with alcohol.

**Thermoplasticity**

Cellulose acetate, when properly plasticized, is a thermoplastic material inasmuch as it will flow when subjected to both heat and high pressure. It is, therefore, considered an ideal substance for plastics, and large quantities are used for this purpose. Its thermoplastic properties are largely due to the presence of plasticizers, unplasticized acetate being useless for thermoplastic moldings, because it does not melt or flow very much below its decomposition temperature without the application of pressure. It begins to decompose slowly above 230° C., and it melts with decomposition between 230 to 260° C. If heated rapidly, for example, by burning, it melts fairly freely; whereas when slowly heated it barely softens before decomposing.

## Viscosity

A solution of cellulose acetate is typically colloidal in nature and, therefore, characterized by a number of properties, of which its viscosity is one of the most important from the practical standpoint. The viscosity of all cellulose derivative solutions, including cellulose acetate, depends upon a number of factors. In most cases the viscosity is largely dependent on the solubility of the cellulose derivative as well as the degree of depolymerization.

The viscosity or consistency of a cellulose acetate in a definite solvent at a given concentration is the deciding factor in selecting the type of cellulose acetate for a specific coating problem. Commercially available cellulose acetate is supplied in a wide viscosity range, from the extremely low viscosity types required for the preparation of spray lacquers to the very high viscosities employed in general plastics work and for some special coating operations.

Those types of cellulose acetate having a viscosity of over 10 seconds have greater tensile strength and flexibility than those having extremely low viscosity.

In many instances it is desired to substitute cellulose acetate for cellulose nitrate because of its improved properties, using a type which does not affect the viscosity. Numerical values in this case have little meaning, as the particular solvent combination employed, as well as the method of determination, will affect the results. A 20 per cent solution of 5-second cellulose acetate in a solvent combination suitable for spray lacquers is approximately equal in viscosity to a 20 per cent solution of  $\frac{1}{2}$ -second nitrocellulose in a solvent combination suitable for the same purpose.

**Determination of Viscosity.** A number of different methods are used for determining this value, the most general of which is the "falling-ball" method. There are a number of variations of this procedure, the Eastman and the modified A.S.T.M. methods being the most common.

*Eastman Method of Viscosity Determination* (9). The sample to be tested is dried in sample drier overnight at 90° to 100° C. To 100 grams of dry cellulose acetate in a one quart screw-top fruit jar is added 400 grams of pure dry acetone. The jar is closed tightly and slowly tumbled end over end for 12 hours in a mechanical tumbling machine.

After the cellulose acetate is thoroughly dissolved, the solution is brought to a temperature of about 20° C., and is poured into a glass cylinder 14 inches high and of an inside diameter of  $1\frac{1}{16}$  inches, having two graduations 10 inches apart, the upper being 2 inches from the top, and the lower 2 inches from the bottom

of the cylinder. The cylinder is placed in a water bath maintained at 20° C. until the temperature of the cellulose acetate solution has become constant and uniform and any bubbles have risen to the surface. It is then placed in such a position that a ball falling through the solution will be visible throughout its passage down the column. A standard steel  $\frac{5}{16}$  inch ball bearing (diam. 0.793 to 0.797 cm.) weighing between 2.033 gm. and 2.035 gm. (obtained from Auburn Ball Bearing Co., Clarissa St., Rochester, New York) is placed on the center of the top surface of the solution in the cylinder and allowed to fall through the center of the solution. The time in seconds required for the steel ball to pass through the 10 inch column of the solution between the two graduations, as measured by a stop watch, is taken as the viscosity in seconds.

*Note:* The acetone used in the above procedure is shaken well with fresh anhydrous calcium chloride and allowed to stand over calcium chloride for at least 2 hours with occasional shaking. It is then distilled from a new batch of calcium chloride in a 22 liter flask using a 36 inch by 1 inch glass tube as a column.

*Modified A.S.T.M. Method of Viscosity Determination.* This method is the same as above with the following important exceptions:

- (1) Temperature is 25° C. instead of 20° C.
- (2) I.D. of tube is 1 inch instead of  $1\frac{1}{16}$  inches.

The higher temperature of the A.S.T.M. method tends to decrease the time required for the ball to pass through 10 inches of solution, while the smaller diameter of the tube increases it. There is no straight line comparison between the two methods, although the A.S.T.M. method roughly gives a 10 per cent higher viscosity in normal ranges than does the Eastman method.

## Acetyl Content

The acetyl content is one of the most important properties of cellulose acetate, and perhaps the least understood by those not closely familiar with cellulose acetate technology. It has an important effect upon the solubility of the material and its tolerance for non-solvents; and upon its resistance, in coated form, to the absorption and to the

TABLE II

SOLUBILITY OF "ACETONE-SOLUBLE" CELLULOSE ACETATE IN SOLVENTS AND DILUENTS

<i>Type of Solvent or Diluent Used in Solution of Cellulose Acetate</i>	<i>Acetyl Content of Cellulose Acetate</i>		
	<i>Low (37.5%)</i>	<i>Medium (38.5%)</i>	<i>High (40.5%)</i>
Ketones .....	C	B	A
Esters (Commercial grades containing more than 5% alcohol) .....	A	B	C
Aromatic hydrocarbons (diluent)	C	B	A
Chlorinated hydrocarbons .....	C	B	A
Alcohols or water (diluent) .....	A	B	C

A—Highest solubility, or highest dilution ratio for diluents.

B—Medium solubility, or medium dilution ratio for diluents.

C—Lowest solubility, or lowest dilution ratio for diluents.

transmission of moisture. The quantitative differences in solubilities of the three standard acetyl types (see Table II) are less in the low viscosity range than in those with viscosity above 15 seconds. The solubility of "acetone-soluble" cellulose acetate of various acetyl contents in solutions containing various solvents and diluents is indicated in a general way in Table II.

The data in Table II indicate that more alcohol or less toluol may be used as a diluent in a solution containing the low acetyl content cellulose acetate than in one containing either the medium or the high acetyl content cellulose acetate. The medium acetyl type will, however, have greatest tolerance for a mixture of 50 per cent alcohol and 50 per cent aromatic hydrocarbon.

Other general effects to be expected on the dried film with the acetyl content are noted in Table III.

TABLE III

THE EFFECT OF WATER ON THE DRIED CELLULOSE ACETATE FILM OF THE THREE TYPES

	<i>Acetyl Content</i>		
	<i>Low</i>	<i>Medium</i>	<i>High</i>
Moisture absorption .....	<i>A</i>	<i>B</i>	<i>C</i>
Moisture transmission .....	<i>A</i>	<i>B</i>	<i>C</i>
Tolerance for water in solvent .....	<i>A</i>	<i>B</i>	<i>C</i>
Weathering .....	<i>C</i>	<i>B</i>	<i>A</i>

*A*—Higher or greater.

*B*—Medium.

*C*—Lower or smaller.

Most tests for the determination of the combined acetic acid are a modification of the Knoevenagel method of alkaline saponification. The results are expressed either as combined acetic acid ( $\text{CH}_3\text{COOH}$ ) or as acetyl ( $\text{CH}_3\text{CO}$ ). For conversion, the acetyl content should be multiplied by  $\frac{60}{43}$  to give the result as acetic acid, and conversely the acetic acid content multiplied by  $\frac{43}{60}$  will give the acetyl content.

More recent tests have been based on the findings of Eberstadt and Knoevenagel (3). Their methods also employ an alkaline saponification. The troublesome difficulties of distillation are eliminated. Little attention is required for routine work, and a large number of samples can be run simultaneously. The Eastman Company modified the original Knoevenagel method to some extent. The method which they use in analyzing cellulose acetate, given in detail below, is accurate to within 0.5 per cent acetyl.

The ester is dried in the 100° C. oven for at least two hours and then placed in a desiccator to cool. Two samples of exactly one gram each are weighed out and placed in 250 cc. Erlenmeyer flasks. The weighings are made to the nearest milligram. To each sample is added 40 cc. of 75% (by volume) ethyl alcohol and the flask is placed in a 55° C. bath (a double-walled bath) for half an hour. 40 cc. of 0.5 normal sodium hydroxide is then added and the flask stoppered loosely with a rubber stopper and replaced in the bath for about 15 minutes, after which the bottle is tightly stoppered and kept at room temperature for 2 days.

One drop of phenolphthalein (1% solution) is added and the excess alkali titrated with 0.5 normal hydrochloric acid. After reaching a temporary end-point, the flask is allowed to stand at least half an hour so that alkali can diffuse from the fibers. The titration is then completed and the total amount of hydrochloric acid is recorded. The percentage of acetyl is calculated by means of the following formula:

$$\% \text{ Acetyl} = \frac{(\text{ml. of NaOH} \times \text{Normality}) - (\text{ml. of HCl} \times \text{Normality}) \times 4.3}{\text{Weight of Sample}}$$

If duplicate determinations differ by more than 0.5% acetyl, the analysis is repeated.

This method requires at least 48 hours and usually longer. At times a more rapid test is desired. This depends upon a rapid saponification, which can be obtained more easily if the cellulose acetate is in solution. The following method gives good results rapidly but is not so accurate as the one recommended.

The cellulose acetate is weighed out using approximately 0.5 gram, and is transferred to a 200–250 cc. Erlenmeyer flask. To the flask are added 20 cc. of pyridine. The flasks are covered with an inverted beaker or loosely stoppered and warmed on a steam bath or in a constant temperature bath (55° C.) until the cellulose acetate has completely dissolved. This should require not more than 15 minutes. Occasional shaking is helpful. Exactly 20 cc. of 0.5 N sodium hydroxide are then added with gentle shaking to prevent the formation of lumps during the precipitation. The flasks are tightly stoppered and placed in a constant temperature bath at 55° C. for half an hour. (A double walled bath in which acetone is kept refluxing is very convenient and maintains a temperature of 55° C.) At the end of this time the sides of the flask are washed down with about 25 cc. of distilled water, two drops of 1 per cent alcoholic phenolphthalein are added and the excess alkali is back-titrated with standard acid. With this method, the tendency of the cellulose to retain the alkali is eliminated. The acetyl pyridine appears to react with the cellulose, especially in the presence of alkali, with resultant high values. Titration should therefore be carried out at

### Precipitation Value

This test is used by Eastman Kodak Company and Tennessee Eastman Corporation (9), in preference to the determination of the acetyl content. The two tests, although entirely different, are a measure of similar properties in the final film, although the precipitation value is much more extensive.

The standard procedure in determining the precipitation value of cellulose acetate is described in detail below:

Five grams of the dry cellulose acetate are accurately weighed and placed in a wide mouth 16 oz. bottle. To this is added 100 cc. of acetone (commercial grade of 99% or better; i.e., sp. gr. at 20° C. 0.788-0.792). The mixture is well stoppered with a rubber stopper and allowed to set at 20° C. until in solution. Solution can be hastened by occasional shaking. To this dope is added slowly (this should require 3 minutes) from a pipette, and with thorough stirring, 150 cc. of a mixture consisting of 2 parts distilled water and 1 part acetone by volume. Care should be taken to keep the solvents and mixtures at 20° C. wherever volumes are being measured.

*Note:* The water and acetone should be accurately measured out and mixed together.

The bottle containing the precipitate and liquid is allowed to settle 12 hours at 20° C. About 25 cc. is centrifuged in stopped tubes at high speed until free from suspended material. Exactly 10 cc. of the clear liquid are removed with a pipette and evaporated to dryness in a tared 50 ml. beaker. If  $W$  is the weight of the residue,

$$\begin{aligned}\text{Ppt. val.} &= 100 - W \left( \times \frac{250}{10} \times \frac{1}{5} \times 100 \right) \\ &= 100 - 500W\end{aligned}$$

*Example:*

$$W = \text{residue} = 0.028 \text{ gram}$$

$$\begin{aligned}\text{Ppt. val.} &= 100 - 0.028 \left( \times \frac{250}{10} \times \frac{1}{5} \times 100 \right) \\ &= 100 - 14 \\ &= 86\%\end{aligned}$$

It can readily be seen that if  $W$  = milligrams of residue,

$$\text{Ppt. val.} = 100 - \frac{W}{2}$$

*Example:*

$$W = 28 \text{ milligrams of residue}$$

$$\begin{aligned}\text{Ppt. val.} &= 100 - \frac{28}{2} \\ &= 100 - 14 \\ &= 86\%\end{aligned}$$

## SOLVENTS

It is said that solvents having an optimum composition with respect to film-forming power give relatively the most waterproof films and



coatings. This should be duly considered in the manufacture of lacquers.

Cellulose acetate will disperse most thoroughly and rapidly if first made up in active solvents in as heavy a solution as the mixing equipment can conveniently handle. The cellulose acetate should be added at a uniform rate *to the solvent*, while the latter is being agitated. After the cellulose has gone into complete solution, the remaining active solvents, together with any or all the diluents, should be added slowly with agitation to prevent the cellulose acetate from precipitating locally.

Small quantities of cellulose acetate solution may be successfully made in bottles, milk cans, or drums by tumbling end over end at a slow speed, normally less than 20 revolutions per minute. Larger quantities may be satisfactorily made in either the turbine or sigma bladed type of completely enclosed mixer.

### Low-Boiling Solvents

The most important and widely used solvent in this class is acetone, which will disperse all the standard types listed. A mixture of methylene or ethylene dichloride and methyl alcohol is a superior solvent and will produce a more flexible cellulose acetate (coating or film) than will acetone. The vapor of these chlorinated hydrocarbons is considered partially toxic and should not be inhaled. Excessive inhalation may be avoided either by coating in a closed system or by proper ventilation. Ethyl acetate (99 per cent) is a fair solvent. Ethyl methyl ketone is somewhat similar to ethyl acetate in its solvent properties. Methyl acetate (99 per cent) is an excellent solvent.

### Medium- and High-Boiling Solvents

Ethyl lactate is a good high-boiling solvent for all standard types of cellulose acetate. Diacetone alcohol is also a solvent for all except the high-acetyl content cellulose acetates, and has a somewhat slower evaporation rate than ethyl lactate. Ethylene glycol monomethyl ether acetate and 1,4 diethylene oxide are good solvents. The use of ethylene glycol monomethyl ether in a solvent combination for cellulose acetate will on an average generally produce a brittle product. Generally it is necessary to use about 10-15 per cent of a high or medium boiler to prevent blushing when coating or spraying cellulose acetate solution in the open air.

Some of the nitroparaffins which have been recently introduced are excellent solvents in combination with alcohols or chlorinated hydro-

carbons for cellulose acetate, cellulose triacetate, and cellulose acetate butyrate. 1- and 2-nitropropane particularly, having an evaporation range closely approximating butyl acetate, will, no doubt, play an important part in the formulations of cellulose acetate and acetate derivative lacquers.

A recent bulletin issued by the manufacturer describes these solvents as follows (1):

"The solvents for cellulose acetate which have been used heretofore are either very rapidly evaporating such as acetone or very slowly evaporating such as ethyl lactate and diacetone. No formulas based on these solvents have given entirely satisfactory results in cellulose acetate lacquers or dopes, since the fast evaporators lead to poor flow and blushing troubles and the slow evaporators greatly delay the final hardening of the film.

"1- and 2-nitropropane have none of these objectionable characteristics. Blended with alcohols the nitropropanes are strong solvents for cellulose acetate, with high tolerances for diluents. Their evaporation rates approximate that of butyl acetate; they have favorable viscosity characteristics; they are non-hygroscopic. Thus for the first time it is possible to formulate cellulose acetate lacquers having the good flow and rapid hardening properties of high-grade nitrocellulose lacquers.

"In preparing a cellulose acetate lacquer with the nitropropanes, it is best to make up a concentrated stock solution containing a high proportion of solvents. This stock solution is then mixed with a thinner containing a high proportion of diluents. Typical solvent formulas for a concentrated stock solution and thinner and for the diluted lacquer appear in the following table:

SOLVENT COMPOSITION

	Concentrated Stock Solution	Thinner	Lacquer at Spraying Viscosity
1-Nitropropane	55%	15%	35%
Butanol	10	20	15
Ethyl alcohol	10	20	15
Toluol	25	45	35

"The solvent mixture recommended for the concentrated stock solution will dissolve the cellulose acetate rapidly and the solution will

have good stability. The composition of the thinner is such that it increases the proportion of alcohols and toluol in the lacquer when it is diluted to spraying viscosity.

"In general cellulose acetate solvent formulas based on 1-nitropropane should contain approximately equal proportions of toluol and of alcohols. Likewise the latter should be divided about equally between butanol and ethyl alcohol. Formulation along these lines will help keep the viscosity of a cellulose acetate lacquer low and the excess tolerance high throughout the drying period.

### Cellulose Triacetate

"Cellulose triacetate lacquers, made from a grade of cellulose acetate containing nearly the theoretical maximum of acetyl radical, yield films which exhibit excellent water resistance, hardness, and resistance to most organic liquids. This cellulose ester has never been widely used, in spite of its technical advantages, primarily because the only effective solvents available were the relatively toxic chlorinated hydrocarbons. It has now been found that large proportions of these chlorinated hydrocarbons can be satisfactorily replaced by mixtures of the nitropropanes with alcohols and aromatic hydrocarbons, thus substantially reducing the toxicity of the solvent mixtures.

"Cellulose triacetate lacquers utilizing the nitropropanes are easily prepared by making a concentrated stock solution with mixtures containing a relatively high proportion of chlorinated solvent. This stock solution is then thinned to spraying viscosity with a mixture containing a high proportion of nitroparaffins, alcohols, and toluol. Typical solvent formulas for such a stock solution and thinner, and for the diluted lacquer, appear in the following table:

SOLVENT COMPOSITION

	Concentrated Stock Solution	Thinner	Lacquer at Spraying Viscosity
1-Nitropropane	45%	45%	45%
Tetrachloroethane	30	..	10
Ethyl alcohol	25	25	25
Toluol	..	30	20

"The stock solution can be thinned without fear of local coagulation if it is stirred reasonably well during the mixing operation. When

formulated in the manner just described the lacquer will be stable on aging and will deposit films of excellent quality. These recommendations apply to the standard grade of cellulose triacetate—that containing about 43.5% acetyl radical. Somewhat lower proportions of tetrachloroethane will suffice for the slightly hydrolyzed grades, which contain about 42.5% acetyl radical. Conversely, slightly more than 10% tetrachloroethane may be needed for the fully acetylated material, which contains 44.4% acetyl radical.”

For cellulose acetate of high acetyl content, the aromatic hydro-

TABLE IV

## SOLUBILITY CHARACTERISTICS OF VARIOUS TYPES OF CELLULOSE ACETATES

<i>Acetyl Value</i> <i>Precipitation Value</i> <i>A.S.T.M.* Viscosity Seconds</i>	37.7–38.4	38.3–39.0	39.6–40.4	38.3–39.0	39.0–39.7	40.0–40.7
	60–65	70–75	70–75	70–75	80–85	88–93
	60–70	55–85	1–4	135–165	88–132	16–33
Solvents	Solubility Characteristics					
<i>Ketones</i>						
Acetone	<i>VG</i>	<i>VG</i>	<i>VG</i>	<i>VG</i>	<i>VG</i>	<i>VG</i>
50% Acetone, 50% methyl alcohol	<i>G</i>	<i>B</i>	<i>B</i>	<i>B</i>	<i>B</i>	<i>VB</i>
Diacetone alcohol	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>	<i>P</i>
Ethyl methyl ketone 89%	<i>G</i>	<i>G</i>	<i>F</i>	<i>F</i>	<i>F</i>	<i>VP</i>
Ethyl methyl ketone 99%	<i>VB</i>	<i>B</i>	<i>G</i>	<i>VB</i>	<i>G</i>	<i>P</i>
<i>Esters</i>						
Ethyl acetate 99%	<i>B</i>	<i>B</i>	<i>G</i>	<i>VB</i>	<i>G</i>	<i>P</i>
Ethyl lactate	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>
Methyl acetate	<i>G</i>	<i>G</i>	<i>G</i>	<i>P</i>	<i>G</i>	<i>G</i>
<i>Glycols</i>						
Ethylene glycol diacetate	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>
Ethylene glycol monomethyl ether	<i>G</i>	<i>G</i>	<i>P</i>	<i>P</i>	<i>P</i>	<i>P</i>
Ethylene glycol monomethyl ether acetate	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>
Ethylene glycol monoethyl ether acetate	<i>VB</i>	<i>B</i>	<i>P</i>	<i>VB</i>	<i>P</i>	<i>B</i>
1,4 Diethylene oxide	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>	<i>G</i>
<i>Chlorinated Hydrocarbons</i>						
Mixture { 80–90% Methylene chloride	<i>E</i>	<i>E</i>	<i>E</i>	<i>E</i>	<i>E</i>	<i>E</i>
20–10% Methyl alcohol						
Mixture { 80–90% Ethylene chloride	<i>E</i>	<i>E</i>	<i>E</i>	<i>E</i>	<i>E</i>	<i>E</i>
20–10% Methyl alcohol						

*E* —Excellent Excellent clarity. Gives films of superior flexibility.

*VG*—Very Good Good clarity and is dispersed rapidly.

*G* —Good Clear homogeneous dope—no grain.

*F* —Fair Completely dispersed, but grainy appearance.

*P* —Poor Solution contains some insoluble material and has tendency to separate into gel layer and liquid layer.

*B* —Bad Appearance of gel or considerable insoluble matter.

*VB*—Very Bad Practically insoluble or gelling.

\* For method determining viscosities—see pages 573 to 574.

carbon type of diluent such as toluene is most satisfactory, and can be added to the greatest extent. The alcohols are much better diluents for the low acetyl content cellulose acetates.

In Table IV are given the solubility characteristics of various types of cellulose acetate as determined by placing two grams of the cellulose acetate in test tubes containing 10 cc. of solvent, allowing them to stand overnight at room temperature, and examining for appearance. In most instances these solutions will be materially improved in appearance by the application of heat and this better appearance may be retained when the material is cooled to room temperature.

The solubility of cellulose triacetate is considerably different from that of commercial acetone soluble acetate types. The solubility characteristics of a commercially available cellulose triacetate having an acetyl content of approximately 43.5 per cent is given in Table V.

### PLASTICIZERS

A study of the literature and patent lists indicates that a host of compounds are recommended for use as plasticizers with cellulose acetate. Some of these compounds are not true solvents for the acetate, but nevertheless are compatible; others can be introduced as plasticizing or pliability agents only with the aid of true plasticizers.

In general, *solvent type* plasticizers will give greater pliability and can be used in fairly large quantities. *Non-solvent type* plasticizers are more effective in maintaining tensile strength and resistance to abrasion. However, smaller quantities must be used. Addition of non-hygroscopic plasticizers to cellulose acetate will materially increase resistance to moisture absorption.

#### The Phthalates

Dimethyl phthalate is used mostly in the plastic field. Its compatibility with cellulose acetate is over 100 per cent, based on the weight of the cellulose acetate: approximately 30 per cent is sufficient to impart good flexibility. It has a relatively high evaporation rate. It is a good solvent for cellulose acetate. It has low acidity and very good heat stability, and has good resistance to the hydrolytic action of boiling water.

Diethyl phthalate is not so good a solvent for cellulose acetate as dimethyl phthalate, although quantities up to 100 per cent may be incorporated. Its vapor pressure and evaporation rate are lower than that of dimethyl phthalate. It has very low acidity and slightly bet-

TABLE V

THE SOLUBILITY CHARACTERISTICS OF CELLULOSE TRIACETATE OF APPROXIMATELY 43.5% Acetyl Content

Parts by Wt. of Solvent to One Part Triacetate	Solvents Tested	Results
10 1	Ethylene chloride Methyl alcohol	Clear solution
10	Methylene chloride	Clear solution
15	Tetrachloroethane	Clear solution
15	Chloroform	Clear solution
15	1 : 4 Dioxane	Clear solution
15	Ethylene chloride	Partial solvent cold Clear solution at 60° C.
10 1	Acetone Methyl alcohol	Slight solvent action
10	Acetone	Slight solvent action
10 0 to 1	Propylene chloride Methyl alcohol	Swelling
10 0 to 15	Methyl alcohol Chloroform	Swelling
10 0 to 1	Ethyl acetate Methyl alcohol	Swelling
10 0 to 4	Ethyl lactate Methyl alcohol	Swelling
10 0 to 8	Methylcellulose acetate Chloroform	Swelling
10	Dichlorodiethyl ether	Swelling
10 0 to 6	Methyl carbitol acetate	Partial swelling

U. S. Patent 2,229,617 describes the use of a mixture of nitromethane and lower saturated monohydric aliphatic alcohol.

ter resistance to the hydrolytic action of boiling water than dimethyl phthalate and about the same as dibutyl phthalate. Diethyl phthalate is a good wetting agent for grinding pigment and therefore a suitable medium to carry pigments and colors into cellulose acetate solutions and plastics.

Dibutyl phthalate is not a solvent for cellulose acetate. Only about 20 per cent to 30 per cent of this material can be used with cellulose acetate. It is an exceptionally stable material with a very low evaporation rate, so that in small quantities it will be retained in the film for a long period of time. It has a higher boiling point than either diethyl or dimethyl phthalate.

The phthalates mentioned are practically clear oily liquids, and are all considered commercially non-toxic. They have excellent stability to ultraviolet light and have a faint odor which is more pronounced in the lower members. They are easily obtained in commercial quantities at reasonable prices.

### The Phosphates

Tributyl phosphate, a fair solvent for cellulose acetate, can be used in quantities up to 100 per cent, with 30 per cent giving good flexibility. It is a good fire retardant. It is practically a colorless and odorless liquid. It has the highest vapor pressure of this group of phosphates and probably the best among the phosphate plasticizers for non-yellowing on sun exposure.

Triphenyl phosphate is a white flaky solid, faintly aromatic in odor, and is a non-solvent for cellulose acetate. It is an excellent fire retardant. It may be used in quantities up to 50 per cent on the weight of the cellulose acetate, and 20 per cent will give fair flexibility. It is practically non-volatile and when used in large quantities will crystallize on the surface of the film. It is therefore not considered a very satisfactory plasticizer for cellulose acetate when used alone. Solvent type plasticizers may be used with triphenyl phosphate to form compatible mixtures with cellulose acetate, and to reduce the tendency to crystallize.

Tricresyl phosphate is an odorless liquid having a very slight yellow color and is a non-solvent for cellulose acetate. It is a very stable ester, non-volatile, and an excellent fire retardant. It should not be used in quantities in excess of 30 per cent of the weight of the cellulose acetate.

All the above phosphates are considered toxic. They should therefore not be used in any cellulose acetate films which may come in

contact with food. The phosphates are comparatively inexpensive and have, therefore, been used for some time with cellulose acetate where fire resistance has been a factor. The two commonly available and useful phosphate plasticizers, namely, tricresyl and triphenyl phosphates, possess very low solubility in water and exceptionally high resistance to the hydrolytic action of boiling water.

### Other Types

Two complex esters of phthalic and glycollic acids, i.e. ethyl phthalyl ethyl glycolate \* and methyl phthalyl ethyl glycolate,† are stated to be solvents for cellulose acetate, to have extremely low rates of evaporation, and to induce good flexibility and plasticity to the composition. They are more compatible with the higher acetyl types of cellulose acetate. They are very good for molding compositions.

Other plasticizers used with cellulose acetate are mixtures of *o*- and *p*-toluene ethyl sulfonamides,‡ butyl phthalyl butyl glycolate,§ and *o*-cresyl-*p*-toluene sulfonate.||

In Table VI is given a list of the tack-free ratios of cellulose acetate with a few plasticizers; i.e., if the plasticizers are present in higher ratios than indicated, the resulting films are tacky.

TABLE VI  
TACK-FREE RATIOS OF ACETATE TO PLASTICIZERS  
Empirical Data

	Cellulose Acetate	Plasticizer
Triacetin	100	65
Dimethyl phthlate	100	125
Diethyl phthlate	100	125
Methyl phthalyl ethyl glycolate *	100	175
Acetyl triethyl citrate	100	175

\* Santicizer M-17.

Triethyl and tributyl aconitates ¶ are recommended for preventing the loss of tensile strength and elongation. Table VII gives some of the newest esters of citric and aconitic acid.

\* Santicizer E-15.

‡ Santicizers 8 and 9.

|| Santicizer 10.

† Santicizer M-17.

§ Santicizer B-16.

(These are all manufactured by the Monsanto Chemical Company.)

¶ Manufactured by Chas. Pfizer Company.



TABLE VII

PLASTICIZING ESTERS OF CITRIC AND ACONITIC ACID FOR CELLULOSE ACETATE

	Compatibility
Triethyl citrate	Good
Tributyl citrate	Fair
Acetyl triethyl citrate	Good
Acetyl tributyl citrate	Fair
Triethyl aconitate	Fair
Tributyl aconitate	Limited
Triethyl tricarallylate	Fair
Tributyl tricarallylate	Limited

Dimethoxy ethyl phthalate (methox) is also a good plasticizer, and it is claimed that cellulose acetate containing this plasticizer does not "sweat."

Sucrose octa acetate is claimed to impart additional water resistance to acetate films.

Tri  $\beta$ -chloroethyl phosphate (Cetamoll Q) is recommended as a plasticizer for further reduction of inflammability and will impart additional fire resistance to acetate cable dopes. Other compatible plasticizers are:

Dicarbitol phthalate (with the aid of heat)	Recommended as plasticizers by the manufacturers of these products.
Methyl orthobenzyl benzoate (Ketone M)	
Glyceryl monophenyl ether	
Glyceryl diphenyl ether	
PHO oil (Manufactured by the Nevilite Co.)	

Triacetin is sometimes used in plastics, and is compatible in all proportions with cellulose acetate. Its resistance to the hydrolytic action of boiling water is extremely poor and for that reason it is not generally recommended.

Castor oil has been used in some cellulose acetate lacquers, mostly as a medium to incorporate pigments, but it is incompatible with cellulose acetate. Acetylated castor oil may be used in very small quantities.

Tables VIII and X give the comparable characteristics of a number of plasticizers with the cellulose acetates. The determination of some of the characteristics are herewith described in detail.

An important factor in the evaluation of plasticizers is the free acidity which may be present in the material, or which may be developed during use or aging.

The amount of *free acidity* in a plasticizer may be conveniently determined by direct titration. The degree of stability of the plasticizers toward development of further acidity during use must be determined by tests designed for that purpose. The results of two such tests are included in Table VIII. These tests indicate the acidity developed in the plasticizers when heated and when refluxed with distilled water. In both tests the free acidity of the original sample is subtracted from the results obtained and the difference recorded in cubic centimeters of normal NaOH required to neutralize 100 grams of plasticizer.

The *heat stability* test involves incubation of the plasticizer for 24 hours at 160° C. to determine the acidity developed at such temperatures. Compounds showing high values in this test should be employed only with care for uses such as molding, extrusion, etc., where temperatures of that order are encountered.

The *stability to moisture* test determines the acidity developed under moist conditions and involves treatment of the plasticizer by refluxing for 24 hours with distilled water.

The *solubility* of cellulose acetate of high, medium, and low acetyl with the plasticizers tabulated was determined by the following tests. One-gram samples of cellulose acetate were mixed with 10 grams of the plasticizer, and after they had stood long enough at the specified temperatures to permit complete penetration were examined and recorded as soluble or insoluble.

Extensive tests have been conducted by Fordyce and Meyer (4) on the behavior of plasticizers with cellulose acetate and cellulose acetate butyrate. Some of their results are listed in Tables IX, X, and XI, together with the experimental procedures.

### Retention of Plasticizer by Cellulose Acetate (Table IX)

Films of known plasticizer content, obtained as described in the preparation of films for compatibility with cellulose acetate, were prepared for retention tests by coating pieces approximately 3 inches (7.6 cm.) square, 0.005 inch (0.127 mm.) thick for roof exposure, oven incubation at 100° C., and water immersion at 40° C.

Roof exposure samples were placed on an out-of-door exposure frame and washed at intervals to remove surface dirt, dried two

TABLE

## SUMMARY OF COMPARABLE CHARACTERISTICS

Plasticizer	Form	Color	Odor	Molecular Weight	Melting Point °C.	Boiling Point °C.	Specific Gravity	Refractive Index	Flash Point °C.
	L = Liquid S = Solid	sl. = slight v.sl. = very slight y. = yellow	sl. = slight v.sl. = very slight						
Benzophenone	S	none	Strong	182	48	305	1.111 <sup>18</sup>	1.602	...
Butyl phthalyl butyl glycolate	L	v.sl.y.	v.sl.	336	-35	219/5 mm.	1.097	1.488	210
Camphor	S	none	Strong	152	178	204	1.000 <sup>0</sup>	...	70
<i>o</i> -Cresyl- <i>p</i> -toluene sulfonate	S	none	v.v.sl.	262	52.5	* Decomp.	1.207 <sup>15</sup>	1.558	...
Diamyl phthalate	L	Yellow	none	306	<-75	342	1.022 <sup>15</sup>	1.488	...
Dibutyl phthalate	L	none	v.sl.	278	-35	325	1.050 <sup>15</sup>	1.490	160
Dibutyl tartrate	LS	none	none	256	22	312	1.098	1.445	160
Dibutyl sebacate	L	sl.y.	sl.	314	-19.5	345	0.933 <sup>15</sup>	1.493	...
Diethoxy ethyl phthalate	S	none	sl.	310	34	345	1.130 <sup>20</sup>	1.492	143
Diethyl phthalate	L	none	v.sl.	222	-0.3	295	1.118 <sup>15</sup>	1.499	140
Diethyl sebacate	L	sl.y.	Strong	258	1.3	308	0.985	1.435	...
Dimethoxy ethyl phthalate	L	none	sl.	282	<-75	209-261/20 mm.	1.17 <sup>20</sup>	1.500	174
Dimethyl phthalate	L	none	sl.	194	0	285	1.193 <sup>15</sup>	1.513	132
Dipropyl phthalate	L	none	sl.	250	31	158/4 mm.	1.077 <sup>25</sup>	1.494	...
Methyl benzoyl benzoate	S	sl.y.	none	240	52	351	1.190	1.587	175
Methyl phthalyl ethyl glycolate	L	sl.y.	v.sl.	266	<-35	189/5 mm.	1.220	1.503	190
<i>o</i> - and <i>p</i> -Toluene ethyl sulfonamide	LS	brown	sl.	199	18	...	1.160 <sup>50</sup>	1.540	...
Tributyl phosphate	L	none	sl.	308	<-20	289	0.976 <sup>25</sup>	1.421	160
Tricresyl phosphate	L	sl.y.	Strong	368	<-35	295/13 mm.	1.175 <sup>20</sup>	1.556	230
Triphenyl phosphate	S	none	v.sl.	326	48.5	245/11 mm.	1.185	1.563	235

\* Decomposes at about 330° C.

hours at 55° C., and weighed. Losses in weight were calculated as plasticizer loss.

Water immersion samples were totally immersed in a constant temperature bath held at 40° C. The water bath was large in proportion to the quantity of film under test, which eliminated the effect of dissolved plasticizer on the leaching action of the water. At intervals the

## VIII

## OF TWENTY CELLULOSE ACETATE PLASTICIZERS (9)

Stability cc. N NaOH/100 g. plasticizer				% Water Solu- bility	Compatibility Parts of Plasticizer per 100 parts Cellulose Acetate			Solvent for Cellulose Acetate S = Solvent N = Non-Solvent					
Free Acid- ity	Additional Acidity Developed		Moisture  Refluxed 24 hr.					High Acetyl 40.5%	Medium Acetyl 39.5%	Low Acetyl 38.5%	High Acetyl 40.5%	Medium Acetyl 39.5%	Low Acetyl 38.5%
	Heat 160°—24 hrs										Temperature °C.		
	CC	Change in Color			25 100 180								
					25 100 180	25 100 180	25 100 180						
0.05	0.00	sl.y.	0.15	0.006	60	50	50	N N N	N N N	S S S			
0.70	4.70	..	34.50	0.018	60	50	25	N N N	N N N	N N N			
0.60	0.50	sl.br.	..	0.170	30	30	30	N N N	N N N	S S S			
0.04	0.06	sl.y.	0.06	0.003	30	40	40	N N N	N N N	N N N			
0.27	2.03	none	0.93	0.010	20	10	10	N N N	N N N	N N N			
0.14	3.46	none	0.16	0.013	30	20	20	N N N	N N N	N N N			
2.75	2.25	br.y.	216.25	0.485	90	90	90	N S S	N S S	S S S			
1.05	5.65	sl.y.	0.05	0.005	<10	<10	<10	N N N	N N N	N N N			
2.15	2.85	yellow	3.05	0.195	70	70	70	N N N	N N N	N N N			
0.07	7.53	none	0.13	0.150	85	85	85	N N S	N N S	N N S			
0.52	12.08	yellow	0.08	0.018	20	10	10	N N N	N N N	N N N			
1.40	1.80	yellow	4.40	0.838	100	100	100	S S S	N S S	N S S			
0.20	0.10	none	1.00	0.305	85	90	90	S S S	S S S	S S S			
0.65	4.75	none	0.15	0.015	75	70	50	N N N	N N N	N N N			
3.20	0.80	brown	1.30	0.005	70	70	70	N S S	N S S	N S S			
2.30	2.90	none	106.20	0.053	>100	>100	>100	S S S	S S S	N S S			
4.30	0.70	black	0.40	0.140	>100	>100	>100	S S S	S S S	S S S			
3.60	1.50	brown	3.50	0.033	70	70	70	N N S	N S S	N S S			
0.55	0.55	..	0.05	0.008	25	20	20	N N N	N N N	N N N			
0.21	0.02	none	0.09	0.002	35	35	30	N N N	N N N	N N N			

samples were washed, dried two hours at 55° C., and weighed, losses in weight being calculated as plasticizer loss. Plasticizers with less than 0.1 per cent loss may be considered quite permanent.

Samples for oven incubation were placed in an oven at 100° C., and after intervals were removed and weighed; losses in weight were calculated as plasticizer loss.

TABLE IX

RETENTION OF PLASTICIZERS BY CELLULOSE ACETATE (ACETYL 40.5 PER CENT) (9)

	Roof, Aug.-Nov.						Oven, 100° C.				Water Bath, 40° C.			
	0	20	60	1	1	3	20	60	100	160	20	60	100	160
	hr.	hr.	hr.	wk.	mo.	mo.	hr.	hr.	hr.	hr.	hr.	hr.	hr.	hr.
Benzophenone	49	45	41	39	..	..	17	12	10	9	19	12	10	8
Butyl phthalyl butyl glycolate	55	55	55	54	53	51	..	24	18	12	49	39	34	28
Camphor	7	5	5	5	..	..	..	..	..	..	3	2	1	0
<i>o</i> -Cresyl- <i>p</i> -toluene sulfonate	35	34	34	32	25	..	24	21	19	14	30	27	26	24
Cyclohexyl- <i>p</i> -toluene sulfonamide	35	32	32	31	31	31	29	27	25	22	29	28	27	26
Diamyl phthalate	19	19	18	18	16	16	15	15	15	14	18	18	17	17
Dibutyl phthalate	32	32	31	30	28	11	20	19	18	17	29	27	26	25
Dibutyl succinate	23	15	9	7	5	3	3	3	3	3	4	1	1	0
Dibutyl tartrate	54	47	43	40	34	6	22	18	17	16	23	21	19	17
Diethoxyethyl adipate	35	22	14	10	9	6	17	9	7	6	5	4	4	3
Diethoxyethyl phthalate	56	48	43	40	38	..	38	..	..	..	25	19	16	14
Diethyl adipate	21	4	3	3	1	..	6	6	6	5	1	0	0	0
Diethylene glycol dipropionate	36	5	4	2	1	..	..	..	..	..	1	1	1	1
Diethyl phthalate	53	41	36	32	30	26	21	18	18	17	26	22	19	14
Diethyl sebacate	17	15	13	12	10	6	7	7	6	6	7	4	3	2
Diethyl succinate	9	3	2	1	0	..	4	3	3	2	0	..	..	..
Diethyl tartrate	49	10	10	9	7	4	16	14	14	12	5	5	4	4
Dimethoxyethyl adipate	53	23	14	10	9	6	18	12	11	8	5	5	5	5
Dimethoxyethyl phthalate	61	53	48	45	41	34	45	38	34	31	28	20	16	14
Dimethyl phthalate	42	29	27	25	24	20	16	14	13	12	17	11	8	6
Dipropyl phthalate	60	53	49	46	37	32	22	21	20	19	33	28	26	24
Ethyl benzoyl benzoate	60	59	59	58	Brittle	..	40	31	28	26	50	46	44	39
Ethylene glycol diacetate	9	3	2	1	0	..	4	3	2	2	0	0	0	0
Ethylene glycol dibutyrate	15	4	3	3	2	..	5	4	4	4	1	0	..	..
Ethylene glycol dipropionate	10	3	2	2	1	..	4	3	3	3	0	0	0	0
Ethyl phthalyl ethyl glycolate	59	57	56	55	53	47	29	27	25	21	38	31	25	21
Methyl benzoyl benzoate	61	57	57	56	Brittle	..	36	33	32	29	52	49	46	42
Methyl phthalyl ethyl glycolate	57	54	53	52	46	43	38	31	29	27	38	29	24	18
<i>o</i> - and <i>p</i> -Toluene ethyl sulfonamide	58	51	49	47	44	40	37	29	26	25	33	24	20	16
Triacetin	43	29	23	20	15	13	14	12	11	10	12	9	8	6
Tributyl citrate	62	58	56	54	50	43	32	25	24	22	34	28	27	24
Tributyl phosphate	40	28	27	23	18	15	14	13	12	12	15	14	12	9
Tributylin	58	49	47	44	37	28	19	18	18	17	25	22	20	17
Tricresyl phosphate	21	21	20	18	18	17	20	19	18	17	18	18	18	17
Triethylene glycol diacetate	51	10	9	8	6	4	14	12	11	10	5	5	5	4
Triethylene glycol dibutyrate	56	32	25	22	17	7	14	12	12	11	6	6	5	5
Triethylene glycol dipropionate	53	22	16	14	11	7	14	11	10	9	6	6	5	4
Triphenyl phosphate	31	29	29	29	28	28	26	23	22	21	27	26	24	23
Tripropionin	55	39	37	34	27	23	19	17	16	14	21	17	15	12

## Compatibility with Cellulose Acetate (Table X)

Samples of film were coated from acetone solutions of cellulose acetate of high (40.5 per cent), medium (38.5 per cent), and low (37.5

TABLE X

COMPATIBILITY OF PLASTICIZERS WITH CELLULOSE ACETATE (9)

	Max. Compatibility *						Max. Permanent Compatibility (High Acetyl)
	Used			Found			
	H	M	L	H	M	L	
<i>Part plasticizer/100 parts cellulose acetate</i>							
Benzophenone	60	60	60	60	50	50	20
Butyl phthalyl butyl glycolate	60	50	30	60	50	25	50
Camphor	30	30	30	30	30	30	5
<i>o</i> -Cresyl- <i>p</i> -toluene sulfonate	30	40	40	30	40	40	30
Cyclohexyl- <i>p</i> -toluene sulfonamide	30	30	30	30	30	30	30
Diamyl phthalate	20	10	10	20	10	10	20
Dibutyl phthalate	30	20	20	30	20	20	30
Dibutyl sebacate	<10	<10	<10	<10	<10	<10	<10
Dibutyl succinate	30	30	20	30	30	20	5
Dibutyl tartrate	90	90	90	90	90	90	25
Diethoxyethyl adipate	40	40	30	40	40	30	5
Diethoxyethyl phthalate	70	70	70	70	70	70	25
Diethyl adipate	90	80	60	65	65	40	0
Diethylene glycol dipropionate	90	90	90	65	65	75	2
Diethyl phthalate	90	90	90	85	85	85	30
Diethyl sebacate	20	10	10	20	10	10	10
Diethyl succinate	100	100	100	20	20	20	0
Diethyl tartrate	100	100	100	90	95	100	5
Dimethoxyethyl adipate	90	90	90	90	90	90	5
Dimethoxyethyl phthalate	100	100	100	100	100	100	25
Dimethyl phthalate	100	100	100	85	90	90	15
Dipropyl phthalate	80	70	50	75	70	50	35
Ethyl benzoyl benzoate	50	50	50	50	50	50	50
Ethylene glycol diacetate	100	100	100	15	15	15	0
Ethylene glycol dibutylate	80	70	60	30	30	35	5
Ethylene glycol dipropionate	100	100	100	15	15	15	0
Ethyl phthalyl ethyl glycolate	100	100	100	100	100	100	40
Methyl benzoyl benzoate	70	70	70	70	70	70	55
Methyl phthalyl ethyl glycolate	100	100	100	100	100	100	40
<i>o</i> - and <i>p</i> -Toluene ethyl sulfonamide	100	100	100	100	100	100	35
Triacetin	100	100	100	95	100	100	12
Tributyl citrate	50	40	30	50	40	30	30
Tributyl phosphate	80	80	80	70	70	70	17
Tributylin	60	40	30	60	40	30	25
Tricresyl phosphate	30	20	20	25	20	20	20
Triethylene glycol diacetate	100	100	100	100	100	95	5
Triethylene glycol dibutylate	70	70	70	70	70	70	7
Triethylene glycol dipropionate	90	90	90	90	90	90	7
Triphenyl phosphate	50	50	45	35	35	40	30
Tripropionin	90	90	90	80	80	85	25

\* H, high acetyl (40.5%); M, medium acetyl (38.5%); L, low acetyl (37.5%).

TABLE XI

SOLUBILITY OF CELLULOSE ACETATE IN PLASTICIZERS (9)

	25° C.			100° C.			180° C.		
	<i>H</i>	<i>M</i>	<i>L</i>	<i>H</i>	<i>M</i>	<i>L</i>	<i>H</i>	<i>M</i>	<i>L</i>
Benzophenone	-	-	-	-	-	-	+	+	+
Butyl phthalyl butyl glycolate	-	-	-	-	-	-	-	-	-
Camphor	-	-	-	-	-	-	+	+	+
<i>o</i> -Cresyl- <i>p</i> -toluene sulfonate	-	-	-	-	-	-	-	-	-
Cyclohexyl- <i>p</i> -toluene sulfonamide	-	-	-	-	-	-	+	+	+
Diamyl phthalate	-	-	-	-	-	-	-	-	-
Dibutyl phthalate	-	-	-	-	-	-	-	-	-
Dibutyl sebacate	-	-	-	-	-	-	-	-	-
Dibutyl succinate	-	-	-	-	-	-	-	-	-
Dibutyl tartrate	-	-	+	+	+	+	+	+	+
Diethoxyethyl adipate	-	-	-	-	-	-	-	-	-
Diethoxyethyl phthalate	-	-	-	-	-	-	-	-	-
Diethyl adipate	-	-	-	-	-	-	+	-	-
Diethylene glycol dipropionate	+	+	-	+	+	-	+	+	+
Diethyl phthalate	-	-	-	-	-	-	+	+	+
Diethyl sebacate	-	-	-	-	-	-	-	-	-
Diethyl succinate	-	-	-	+	+	-	+	+	+
Diethyl tartrate	+	+	+	+	+	+	+	+	+
Dimethoxyethyl adipate	-	+	+	+	+	+	+	+	+
Dimethoxyethyl phthalate	+	-	-	+	+	+	+	+	+
Dimethyl phthalate	+	+	+	+	+	+	+	+	+
Dipropyl phthalate	-	-	-	-	-	-	-	-	-
Ethyl benzoyl benzoate	-	-	-	-	-	-	+	+	+
Ethylene glycol diacetate	+	+	+	+	+	+	+	+	+
Ethylene glycol dibutylate	-	-	-	-	-	-	-	-	-
Ethylene glycol dipropionate	-	-	-	+	+	-	+	+	+
Ethyl phthalyl ethyl glycolate	-	-	-	-	-	-	+	+	+
Methyl benzoyl benzoate	-	-	-	+	+	-	+	+	+
Methyl phthalyl ethyl glycolate	+	+	-	+	+	-	+	+	+
<i>o</i> - and <i>p</i> -Toluene ethyl sulfonamide	+	+	+	+	+	-	+	+	+
Triacetin	+	+	+	+	+	-	+	+	+
Tributyl citrate	-	-	-	-	-	-	-	-	-
Tributyl phosphate	-	-	-	-	+	-	+	+	+
Tributylin	-	-	-	-	-	-	-	-	-
Tricresyl phosphate	-	-	-	-	-	-	-	-	-
Triethylene glycol diacetate	+	+	+	+	+	-	+	+	+
Triethylene glycol dibutylate	-	-	-	-	-	-	-	-	-
Triethylene glycol dipropionate	-	-	-	-	-	-	+	+	+
Triphenyl phosphate	-	-	-	-	-	-	-	-	-
Tripropionin	-	-	-	-	-	-	+	+	+

*H*, high acetyl (40.5%); *M*, medium acetyl (38.5%); *L*, low acetyl (37.5%).  
 + Soluble. - Insoluble.

TABLE XII  
THE CHEMICAL AND PHYSICAL EFFECT OF PLASTICIZERS FOR CELLULOSE  
ACETATE (5)

Material and Chemical Name	Solvent Power	Water Resistance	Oil Proofness	Discoloration Heat and Light	Remarks
Dimethyl phthalate	Excellent 52-60% acetic C.A.	Fair	Fair	Good	Toughens; volatile in lacquers; often used in plastics.
Diethyl phthalate	Good 52-58% acetic	Fair	Fair	Good	Toughens; volatile in lacquers; often used in plastics.
Methox—dimethyl cello-solve phthalate	Good 52-58% acetic	Fair-Poor	Good	Good	Toughens; not volatile; toxic internally.
Diphenyl phthalate (solid)	Poor—com- patible to 15% of C.A.	..	..	..	Alcohol-resisting; stiffener; makes films casting films.
Dibutyl phthalate } Diamyl phthalate }	Poor—10% compatible with 53% acetic; 15% 58% acetic	Fair	Fair	Good	Used with dimethyl phthalate to reduce warping and shrink- ing; may sweat.
Santicizer M-17—methyl phthalyl ethyl glycolate	Good 53-58% acetic	Good	Good	Good	Less volatile; for lacquer.
Santicizer E-15—ethyl phthalyl ethyl glycolate	Good 53-58% acetic	Good	Good	Good	Less volatile; for lacquer.
Santicizer 8—p-toluene sulfonamid	Good 52-59% acetic	Good	..	Fair	Lower melting point; blush in humid conditions; harden surfaces.
Santicizer 9—ethyl p-toluene sulfonamid (solid)	Good	Good	..	Fair	Lower melting point; blush in humid conditions; harden surfaces.
Santicizer 10—ethyl p-toluene sulfonate	Good	Fair	..	Poor	Lower melting point; blush in humid conditions; harden surfaces.
Triphenyl phosphate (solid)	Poor—C.A. 58% acetic Fair—C.A. 53% acetic	Good	Good	Fair- Good	Flameproof; stiffener; non- volatile; may be toxic.
Tributyl phosphate	Fair—53-58% acetic	Fair	Good	Good	Flame resisting; volatile.
Dibutyl tartrate	Good—52-58% acetic	Poor	Good	Fair	Volatile.
Diamyl tartrate	Good—52-58% acetic	Poor	Good	Fair	Volatile.
Camphor (solid)	Non-solvent compatible	Good	Fair	Fair	Stiffener; volatile; promotes surface hardness, compatibil- ity of triphenyl phosphate and adhesion.
Triacetin	Excellent all acetics	Poor	Good	Good	Volatile; tends to hydrolyze; toughens.
Tripropionin	Fair—Good 52-58% acetic	Fair	Good	Good	Less volatile than triacetin; toughens.
KP-45—diethylene glycol dipropionate	Good 52-58% acetic	Poor	Good	Good	Volatile; toughens; softens plastics.
Acetyl triethyl citrate	Good	Fair	Good	Good	Less volatile than dimethyl phthalate; gives tough plastics.
Triethyl citrate	Good 52-58% acetic	Poor	Good	Fair	More volatile.
Sucrose octa-acetate (solid)	Compatible	Fair	Fair	Fair	Stiffener; non-volatile; embrit- tles; adhesion.



per cent) acetyl contents containing increasing quantities of each plasticizer. The films were examined after evaporation of the solvent to determine the maximum quantity of plasticizer which would give a clear film. Films of this maximum plasticizer content were then prepared, and, after complete curing by incubation for 18 hours in an oven at 55° C., the plasticizer contents were determined by analysis. Agreement on duplicate tests was found to be reliable within 5 per

TABLE XIII

COMPATIBILITY OF SOME RESINS WITH CELLULOSE ACETATE (9)

Type of Cellulose Acetate	* Viscosity: 2-5, Acetyl content % 39.6-40.4		* Viscosity: 50-80, Acetyl content % 38.3-39.0		* Viscosity: 80-120, Acetyl content % 39.0-39.7		† Viscosity: 4-8, Acetyl content approx. 43.5%	
Parts Plasticizer per 100 Parts Cellulose Acetate-Plasticizer Used = Diethyl Phthalate	0	15	0	15	0	15	0	15
<i>Resin Tested</i>								
Rezyl 14 †	20	30	10	I	10	30	30	30
" 12	I	I	I	I	I	I	I	I
" 99-4	I	I	I	I	I	I	I	I
" 19	I	I	I	I	I	I	I	I
" 22	I	I	I	I	I	I	I	I
Rezyl X-315	I	I	50	80	20	20	100	100
" 1102	I	I	I	I	I	I	Haze	50
" 869	I	I	I	I	I	I	I	20
" 807	I	I	I	I	I	I	I	30
" 829	I	I	I	I	I	I	I	20
" 412-1	I	I	I	I	I	I	I	10
" 775-4	I	I	I	I	I	I	I	I
Glyceryl Phthalate §	100	100	100	100	100	100	100	100
Glycol Phthalate	100	100	100	100	100	100	20	100
Santolite X	100	100	100	100	100	100	100	100
" MS	100	100	100	100	100	100	100	100
" MHP	100	100	100	100	100	100	100	100
" MH	100	100	100	100	100	100	100	100
Acryloid C10 ¶	20	80	I	10	30	I	80	10
" B7	10	20	I	10	20	30	80	30
" A10	30	I	30	I	30	20	100	50

\* For method of determining viscosities see section on viscosity.

† Viscosity is determined in a 20 per cent solution in a solvent mixture composed of 90 per cent methylene chloride and 10 per cent methyl alcohol, and is measured by the time required for a 3/16-inch steel ball to fall through 10 inches of solution in a 1 1/16 inch tube at 20° C.

‡ American Cyanamid Co.

§ Glyco Products Co.

|| Monsanto Chemical Co.

¶ Resinous Products Co.

TABLE XIV  
 PROPERTIES OF CELLULOSE ACETATE LACQUER FILMS (5)

Parts	Film Composition		Water * Spot Test	Unsalted Butter Test †		50% (vol.) Alcohol Test ‡	
	Parts and Plasticizer Used	Parts and Resin Used		Rusting	Coating	Rusting	Coating
LL-1 C.A.							
10	0 ..	0 ..	V.B.	V.B.	Sl.soft	Sl.	Soft
10	2 Dimethyl phthalate	0 ..	V.B.	V.Sl.	OK	V.Sl.	Soft
10	4 Dimethyl phthalate	0 ..	V.B.	V.Sl.	OK	Sl.	Soft
10	2 Dimethyl phthalate	3 Rezyl 14	Sl.	Sl.	P.Adh.	V.Sl.	Soft
10	4 Dimethyl phthalate	3 Rezyl 14	Sl.	None	P.Adh.	Sl.	Soft
10	2 Santicizer M-17	0 ..	V.B.	Sl.	P.Adh.	Sl.	Soft
10	4 Santicizer M-17	0 ..	V.B.	Sl.	P.Adh.	Sl.	Soft
10	2 Santicizer M-17	3 Rezyl 14	Sl.	Sl.	P.Adh.	Sl.	Soft
10	4 Santicizer M-17	3 Rezyl 14	Sl.	Sl.	P.Adh.	Sl.	Soft
10	2 Santicizer 8	0 ..	V.B.	V.B.	Soft	Sl.	Soft
10	4 Santicizer 8	0 ..	V.B.	V.B.	Soft	Sl.	Soft
10	2 Santicizer 8	3 Rezyl 14	Sl.	Sl.	Soft	Sl.	Soft
10	4 Santicizer 8	3 Rezyl 14	Sl.	Sl.	Soft	Sl.	Soft
10	2 Triphenyl phosphate	0 ..	V.B.	Sl.	OK	Sl.	Soft
10	4 Triphenyl phosphate	0 ..	B.	Sl.	OK	Sl.	Soft
10	2 Triphenyl phosphate	3 Rezyl 14	Sl.	Sl.	P.Adh.	Sl.	Soft
10	4 Triphenyl phosphate	3 Rezyl 14	Sl.	Sl.	P.Adh.	Sl.	Soft
10	2 Acetyl triethyl citrate	0 ..	V.B.	V.B.	OK	Sl.	Soft
10	4 Acetyl triethyl citrate	0 ..	V.B.	V.B.	OK	Sl.	Soft
10	2 Acetyl triethyl citrate	3 Rezyl 14	Sl.	Sl.	P.Adh.	V.Sl.	Soft
10	4 Acetyl triethyl citrate	3 Rezyl 14	Sl.	Sl.	P.Adh.	V.Sl.	Soft
10	2 Diphenyl phthalate	0 ..	V.B.	V.B.	Soft	V.Sl.	Sl.soft
10	4 Diphenyl phthalate	0 ..	V.B.	V.B.	Soft	V.Sl.	Sl.soft
10	2 Diphenyl phthalate	3 Rezyl 14	Sl.	Sl.	Soft	Sl.	Sl.soft
10	4 Diphenyl phthalate	3 Rezyl 14	V.Sl.	Sl.	Soft	Sl.	Sl.soft
10	2 Diphenyl phthalate	3 Bakelite XR-3180	V.B.	V.B.	Soft	B.	Sl.soft
10	4 Diphenyl phthalate	3 Bakelite XR-3180	B.	B.	Soft	Sl.	Sl.soft
10	2 Diphenyl phthalate	3 Bakelite XR-4357	Sl.	Sl.	Soft	V.Sl.	Sl.soft
10	4 Diphenyl phthalate	3 Bakelite XR-4357	Sl.	Sl.	Soft	V.Sl.	Sl.soft
10	2 Diphenyl phthalate	3 Gelva V 2½	V.B.	Sl.	Soft	V.Sl.	Sl.soft
10	4 Diphenyl phthalate	3 Gelva V 2½	V.B.	Sl.	Soft	V.Sl.	Sl.soft
RS ½ Sec. N/C—							
10	0 ..	0 ..	V.Sl.	V.Sl.	Soft	B.	OK
10	4 Dibutyl phthalate	0 ..	Sl.	V.Sl.	Soft	V.Sl.	OK
10	4 Dibutyl phthalate	3 Rezyl 14	V.Sl.	None	Soft	Sl.	OK
10	4 Raw castor oil	0 ..	Sl.	Sl.	Soft	V.Sl.	OK
10	4 Raw castor oil	3 Rezyl 14	V.Sl.	None	Soft	Sl.	OK
Hercoese C (30 cps.)							
10	0 ..	0 ..	B.	Sl.	Sl.soft	B.	OK
10	4 Dimethyl phthalate	0 ..	B.	Sl.	Soft	Sl.	Soft
10	4 Dimethyl phthalate	4 Rezyl 14	B.	Sl.	Soft	B.	Soft
Chlor. Rub- ber 20 Cps.							
10	0 ..	0 ..	V.Sl.	None	Dis- solved	V.Sl.	P.Adh.
10	5.3 Dibutyl phthalate	4 Teglac 15	None (White coating)	None	Dis- solved	None	Soft
10	2.5 Dibutyl phthalate	5 Rezyl 869	V.Sl.	V.Sl.	OK	B.	OK

Symbols: Sl. = Slight V. = Very B. = Bad P.Adh. = Poor Adhesion

\* Film sprayed, air-dried 2 days, kept in contact with water for 24 hours at room temperature; note rusting, etc.

† Same film in contact with unsalted butter 24 hours; note rusting, softening on area of contact.

‡ Same film in contact with alcohol 24 hours; note rusting and softening of film.

cent, and results here obtained were therefore rounded off to the nearest even 5 per cent plasticizer content as the maximum compatibility.

### **Solubility of Cellulose Acetate in Plasticizers (Table XI)**

The solubility was determined of cellulose acetate of high, medium, and low acetyl values. One-gram samples of cellulose acetate were mixed with 10 grams of the plasticizer and, after they had stood long enough at the specified temperature to permit complete penetration, were examined and recorded as soluble or insoluble.

### **Resin Compatibility**

Cellulose acetate is very limited in its compatibility with natural or synthetic resins. Among the natural resins, accroides, elemi, guaiac, mastic, and sandarac resins are compatible. These resins have very limited practical value in the present-day lacquer industry; therefore, we resort to the use of specially prepared synthetic resins. The types given in Table XIII represent the limited list of compatible materials.

Observations for Table XIII were made on thin films cast on glass from an active solvent. Limit of compatibility is noted as that composition of film which, when cast from an active solvent, dries free of a resin blush or haze. Examination of film was made after film had had sufficient time thoroughly to dry free of solvent.

The number indicates the parts of resin per 100 parts of cellulose acetate that are compatible.

I—Incompatible at the lowest amount resin used (10 parts).

The highest amount of resin tested—100 parts.

In Table XIV we list some of the characteristics of cellulose acetate with plasticizers and resins and the resistance of such films.

## **INDUSTRIAL USES**

The commercial use of cellulose acetate for lacquers is very limited for many reasons, the most important of which are limited solvency, lack of compatible resins, and the availability of cellulose nitrate. With the exception of stability, light resistance, and non-flammability, cellulose nitrate is superior in all characteristics to cellulose acetate, since it is much cheaper, has a wider range of solubility in useful solvents, which favorably influences film formation, and a high degree of tolerance for non-solvents, resins, and plasticizers.

For this reason the lacquer formulator will consider the use of cellulose acetate as a film-forming ingredient in place of nitrocellulose usually only where the following characteristics are desired:

1. Stability (aging, decomposition, and heat).
2. Resistance to sunlight discoloration and transmission of ultra-violet rays.
3. Non-flammability.
4. Finishes resistant to solvents where cellulose nitrate because of its composition might not be suitable.
5. Resistance to certain chemicals and materials.

The principal uses for cellulose acetate are in the rayon, plastic, photographic film, sheeting, wrapping, and protective coatings fields. Among the many suggested uses for cellulose acetate in the protective coating field are:

Airplane dopes.	Artificial leather.	Shower curtains.
Cable lacquers.	Shade cloth.	Window curtains.
Coated textiles.	Finish for light bulbs.	Wallpaper.
Food containers.	Labels.	Pencil lacquer.
Wire lacquer.	Furniture lacquer.	Chicken wire glass.

Cellulose acetate has been used in the past in considerable quantity as a dope finish for airplane fabrics. It is still in use but only as a protective layer over nitrate dopes on certain parts of the airplanes. Because of its chemical composition, cellulose acetate is inherently poorer in water resistance than other cellulose derivatives, and, because it absorbs water, airplanes finished with acetate dope lose their tautness in humid weather to such an extent that the airplane fabric sags considerably.

Unquestionably great improvement has been made since the First World War to stabilize cellulose acetate and make it more soluble in organic solvents. Nevertheless, it is still unsuitable for dopes, and until a plasticizer is discovered which will overcome the lack of water resistance of the acetate there is not much chance of further inroads being made with this product in the airplane finishing industry.

Fortunately, some of the newest mixed esters, namely a special type of cellulose acetate butyrate, seem to fill the need for a fireproof finish for airplanes. Recent investigation indicates that cellulose triacetate possesses very good properties for retaining tautness. It could not be used in the past because of high viscosity. Lately, however, it is also manufactured in the lower viscosity ranges, and the only reason it is not used for dopes or other industrial applications is because of its poor solubility in commercially available organic solvents.

A very useful application for this product is chicken wire glass, which is made by dipping and slowly withdrawing wire mesh from a

plasticized acetate solution. This forms a continuous film all around the wire mesh, closing the interstices of it, resulting in a flexible product which is readily rolled for shipment. It is used for housing chickens and permits transmission of the health-giving and beneficial ultra-violet rays of the sun. Two parts of cellulose acetate and one part of methyl phthalyl ethyl glycollate \* give a satisfactory finish for this purpose.

A fire-resistant acetate coating can be made by using 20 per cent or more of triphenyl phosphate, based on cellulose acetate. The introduction of methyl phthalyl ethyl glycollate will improve the flexibility at the expense of fire resistance.

The adhesion of acetate lacquers is increased by the addition of toluene-sulfonamide-formaldehyde resins.

The following formula is suggested for a coating or impregnating composition:

Cellulose acetate .....	100
Dibutyl tartrate .....	150
Triphenyl phosphate .....	15

Dissolve in proper solvents.

Heat-resistant clears for application on metals or other surfaces which will not yellow at elevated temperatures are achieved with cellulose acetate base materials. Additional heat resistance is secured by adding metallic salts of naphthanic acids as follows:

Cellulose acetate .....	100
Ethyl paratoluene sulfonamide ..	25
Triphenyl phosphate .....	12.5
Dimethyl phthlate .....	2.5
Calcium naphthanate .....	0.05 (7)

Cellulose acetate was used for quite some time in the manufacture of safety glass, but has now been partly replaced by vinyl resins.

A few typical formulations for acetate lacquer are given herewith (5):

CABLE LACQUER		AIRPLANE DOPE	
Lacquer acetate (high viscosity) ..	8.0	Cellulose acetate .....	9.0
Triphenyl phosphate .....	3.0	Triphenyl phosphate .....	1.0
Tributyl phosphate .....	7.0	Diacetone alcohol .....	9.0
Santicizer M-17 .....	2.0	Ethyl acetate .....	22.5
Acetone .....	52.0	Toluene .....	13.5
Alcohol .....	10.0	Acetone .....	18.0
Toluene .....	8.0	Methyl ethyl ketone .....	27.0
Ethyl lactate .....	10.0		
	100.0		100.0

\* Santicizer M-17.

SPRAYING LACQUER		SPRAYING LACQUER	
Cellulose acetate .....	7.0	Cellulose acetate .....	7.0
Rezyl 14 .....	2.1	Rezyl 14 .....	2.1
Santicizer M-17 .....	2.1	Santicizer M-17 .....	2.6
Acetone .....	46.8	Nitromethane .....	20.1
Methyl acetate .....	8.3	1-Nitropropane .....	14.4
Ethyl lactate .....	8.3	Ethanol .....	14.4
1-Nitropropane .....	6.8	Butanol .....	3.8
Butanol .....	1.4	When dissolved add, while stirring,	
When dissolved add, while stirring,		Methyl acetate .....	9.6
Methyl Cellosolve acetate .....	3.9	Toluol .....	26.0
Toluol .....	13.3		
	100.0		100.0

*Note:* This formula has withstood 4 months' outdoor weathering on polished steel with only slight rusting.

*Note:* This solvent mixture will dissolve cellulose acetate of acetic content as high as 59.0%.

PAPER COATING LACQUER		PAPER COATING LACQUER	
Cellulose acetate .....	13.3	Cellulose acetate .....	20.0
Santicizer M-17 .....	6.7	Santicizer M-17 .....	10.2
Santicizer 8 .....	1.6	Santicizer 8 .....	2.5
Acetone .....	20.0	Methyl ethyl ketone .....	37.0
Methyl ethyl ketone .....	8.3	Acetone .....	16.3
1-Nitropropane .....	40.6	Methyl Cellosolve acetate .....	7.0
2-B Alcohol .....	9.5	Ethyl lactate .....	7.0
	100.0		100.0

PENCIL LACQUER		CLOTH-FINISHING LACQUER	
Lacquer acetate (low viscosity) .	20.0	Film acetate (medium viscosity)	10.0
Triphenyl phosphate .....	3.0	Tributyl phosphate .....	2-5
Santolite MHP .....	3.0	Diethyl phthalate .....	2-5
Santicizer M-17 .....	3.0	Acetone .....	50-56
Acetone .....	46.0	Ethyl acetate .....	15
Ethyl acetate .....	25.0	Methyl Cellosolve .....	15
	100.0		

WIRE-COATING LACQUER		WIRE-COATING LACQUER	
Acetone .....	53.0	Acetone .....	40.0
Ethyl acetate .....	7.0	Ethyl acetate .....	10.0
Methyl Cellosolve .....	5.0	Ethyl lactate .....	10.0
Cellulose acetate .....	14.0	Toluene .....	10.0
Triphenyl phosphate .....	10.5	Cellulose acetate .....	15.0
Diethyl phthalate .....	10.5	Diethyl phthalate .....	7.5
		Rezyl 337-1 .....	7.5
	100.0		

The preceding lacquers may be thinned to the consistency desired with the following thinner:

Methyl Ethyl Ketone...	30
Acetone .....	40
Ethyl lactate .....	10
Ethyl acetate .....	10
Toluene .....	10

In mixing compositions such as those suggested above, better results will be obtained if the entire solvent combination is not added at one time. This is especially true if a lean solvent combination is used. The general practice is to employ, for actual dissolving operations, all the solvents specified and only a small amount of the diluent. When the cellulose acetate is completely in solution, the remainder of the solvent combination (containing all the diluents) is added slowly with constant mixing. Care should be taken that the diluents are not added so fast that the material precipitates at any point.

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## CHAPTER 20

### CELLULOSE MIXED ESTERS, CELLULOSE ACETATE BUTYRATE AND CELLULOSE ACETATE PROPIONATE

MICHAEL A. DORIAN

#### HISTORY AND GENERAL CHARACTERISTICS

Through substitution of an appreciable amount of the butyryl or propionyl radical for the acetyl in the triester of cellulose acetate, the resulting products are more readily soluble in the commercially available solvents than cellulose acetate. Both these products have been available to industrial lacquer users since 1935. They are white granular materials with practically no odor and give solutions of excellent clarity and color. These materials are superior for use in lacquer, not only because of their better solubility in solvents but also because the moisture absorption is considerably less than that of cellulose acetate. Lacquers having good resistance to outside exposure and fair adhesion to metal surfaces may be prepared from some of these mixed esters.

Because their resistance to ultraviolet light and flammability is on a par with cellulose acetate, they are truly much better tools in the hands of the lacquer formulator for the production of industrial coatings than cellulose acetate. Although cellulose acetate has been available to the lacquer industry for decades, these two compounds are probably used in greater amount for industrial lacquer application than the cellulose acetate, except in textiles where the use of cellulose acetate is considerably greater. Owing to its superior resistance to the absorption of water vapors, cellulose acetate butyrate compositions have replaced acetate dopes in the airplane industry.

Table I gives the types available to the industry and some of their properties.

In Table II are compared some properties of the most commonly used cellulose esters.

In Table III are shown the relative solubilities of the medium-viscosity standard types mixed esters.



TABLE I  
TYPES OF MIXED ESTERS AND PROPERTIES (5)

Name	Cellulose Acetate Propionate	Cellulose Acetate Butyrate	
	C.A.P., Type I	C.A.B., Type I	C.A.B., Type II
Acetyl content	14-17%	30½-33%	12-15%
Propionyl content	30-33%	<0.5%	<0.5%
Butyryl content	<0.5%	14-17%	35-38%
Softening range	210-230° C.	230-250° C.	190-210° C.
Specific gravity	1.24	1.25	1.21

TABLE II  
SOME PROPERTIES OF THE MOST COMMONLY USED CELLULOSE ESTERS

	Cellulose Acetate Butyrate	Nitro- cellulose	Cellulose Acetate	Cellulose Acetate Propionate
Moisture Permeability (gm. H <sub>2</sub> O/cm./cm. <sup>2</sup> hr. at 22° C. saturated air) × 10 <sup>-6</sup>	4.0-5.0	2.4	6.0-8.0	4.0-5.0
Moisture Absorption, % (at 85% R. H. and 22° C.)	3.0-3.3	3.1	8.0	3.0-3.2
Tensile Strength Breaking load-kg./cm. <sup>2</sup> (22° C. 60% R.H., 45 kg./cm. <sup>2</sup> min. load- ing rate)	400-550	600-800	500-600	
Breaking Elongation	3.5-4.0%	4-6%	2-4%	

The study of the solubility table brings out the interesting fact that as the butyryl content increases against the acetyl content, the solubility becomes greater, while the softening range is decreased. This high butyryl content product closely approaches the general solubility characteristics of nitrocellulose in ester solvents. In fact, it is soluble in solvents in which nitrocellulose is not, for example, an equal mixture of low-boiling alcohols and coal tar naphthas.

TABLE III  
RELATIVE SOLUBILITIES OF MIXED ESTERS (5)

Solvent	Medium Viscosity Type of Mixed Esters		
	C.A.B., Type I	C.A.B., Type II	C.A.P., Type I
Acetone	S	S	S
Methyl ethyl ketone	S	S	S
Methyl <i>n</i> -butyl ketone	I	S	I
Diacetone alcohol	S	S	S
1 : 4 Dioxane	S	S	S
Methyl acetate 88%	S	S	S
Ethyl acetate 88%	S	S	S
Butyl acetate 88%	SW	S	S
<i>iso</i> -Amyl acetate 88%	I	S	SW
Cellosolve acetate	S	S	S
Methyl Cellosolve acetate	S 60° C.	S	S
Ethyl lactate	S	S	S
1- and 2-Nitropropane	S	S	S
Methylene dichloride	S	S	S
Ethylene dichloride	S	S	S
Propylene dichloride	I	S	S
50% Toluene—50% methyl alcohol	SW	S	S
50% Toluene—50% ethyl alcohol	I	S	S
50% Benzene—50% methyl alcohol	SW	S	S
50% Benzene—50% ethyl alcohol	SW	S	S
80% Ethylene dichloride } 20% Ethyl alcohol }	S	S	S

S—Soluble at room temperature unless otherwise noted.

I—Insoluble.

SW—Swelling.

The recently introduced 1- and 2-nitropropanes are excellent solvents as described by the manufacturer (1).

"Cellulose acetobutyrate—particularly the grade containing approximately 31% acetyl radical and 16% butyryl—is of considerable interest in lacquers and dopes because of its high water resistance, compatibility with plasticizers, and resistance to ultraviolet light. Its films have the further advantages of low inflammability, good resis-

tance to yellowing, and excellent hardness. However, like cellulose acetate, its use has been limited by the lack of suitable medium-boiling solvents and by its incompatibility with most resins. Now, with the nitropropanes, cellulose acetobutyrate lacquers can be formulated which not only have excellent flow but also may contain any of a number of the common resins.

"The solvent power of 1- and 2-nitropropane for cellulose acetobutyrate compares favorably with that of butyl acetate for nitrocellulose. For example, nitropropane solutions of cellulose acetobutyrate have approximately the same tolerances for toluol and for ethyl alcohol as do butyl acetate solutions of nitrocellulose. Moreover, the tolerances of such nitropropane solutions are much higher for mixtures of ethyl alcohol and toluol than for either material alone. As cellulose acetobutyrate solvents the nitropropanes, although medium-evaporating, have the striking advantage that they produce viscosities little higher than those obtained with rapidly evaporating solvents such as acetone.

"To insure easy and rapid solution of the cellulose acetobutyrate, it is best to make a concentrated stock solution containing a high proportion of nitropropane. This stock solution is reduced to spraying viscosity with a thinner containing high proportions of alcohols and toluol.

"Typical solvent formulas for a concentrated stock solution, thinner, and diluted lacquer appear in the following table:

SOLVENT COMPOSITION

	Concentrated Stock Solution	Thinner	Lacquer at Spraying Viscosity
1- or 2-Nitropropane	45%	5%	25%
Butanol	5	15	10
Ethyl Alcohol	15	15	15
Toluol	35	65	50

"Although less than 25% of nitropropane is required with certain more soluble grades of cellulose acetobutyrate, the formula shown above will serve as an excellent starting point in developing a satisfactory lacquer.

## RESINS

The compatibility of the commercially available types of cellulose acetate butyrates with resins does not approach the wide compatibility of the nitrates, and lies between the nitrate and the acetate—closer to the acetate in this respect.

There has been considerable dispute regarding the compatibility of gums and resins with the various types of mixed esters. In some instances, tables of compatibilities have been made from the result of a single series of experiments. Furthermore, such compatibilities may be greatly influenced by the kind of solvents used in the tests, as well as the amount and kind of plasticizer. For example, solutions made with solvent mixtures containing high percentages of 1- or 2-nitropropane and aromatic hydrocarbons will produce clear lacquers containing resins that would be incompatible with other solvent combinations.

The dryness of the solvents, in some instances, has a decided effect on the compatibility of the gum with the mixed esters.

The following gums are apparently compatible to a considerable degree with the mixed esters, C.A.B., Type I, C.A.B., Type II, and C.A.P., Type I.

Red gum (Yucca)	Bakelite XR 4503
Gum guaiac	Bakelite 4036
Vinsol resin *	Bakelite 3180
Hydrogenated methyl abietate	Acryloid C10
(Hercolyn *)	Acryloid B7
Methyl abietate	Rezyl 337-2
(Abalyn *)	Durez 500
Neville Hard	Durez 525
Rezyl 14	Durez 550
Santolite MS	Amberol 226
Santolite MH	Aroclor 1262
Santolite MHP	Gelva 2½

In addition to the above, the following resins are compatible to a lesser degree. In general, all resins are more compatible with cellulose acetate butyrate type II than with other mixed esters on the market at the present time.

Gum elemi	Acryloid A10
Dammar (Singapore)	Cumar MS

\* Trade mark, Hercules Powder Company.

Balsam	Rezyl 53 *
Rosin A1	Superbeckacite 1001 *
Neville PHO	Duraplex ND-75 *
Teglac 15	Beckosol 1323 *
Bakelite BR 254	Aroclor 4465 *

Information available at the present time merely indicates that the resins mentioned may be compatible and may be useful when formulated in certain lacquers for specific purposes. Furthermore, certain resins such as ester, dammar, and elemi apparently vary in composition so that material received from various manufacturers show different compatibilities, some being entirely insoluble and others being compatible to as much as 40 parts per 100 without blush.

A great deal of work is yet to be done to determine the usefulness of the various types of resins in specific formulations. Some resins may improve properties such as gloss, hardness, adhesion, and resistance to moisture absorption. It is true, however, that certain other resins are used merely as fillers and may impart undesirable properties to the lacquers, such as brittleness and poor weather resistance.

### PLASTICIZERS

Cellulose acetate butyrate and acetate propionate are plasticized much more readily than nitrocellulose, and the resulting film using an identical amount of plasticizer is much softer. They are compatible with almost all the commercially available chemical plasticizers of the ester types but are not miscible with oils, either raw or treated, unless an excessive amount of chemical plasticizer is used. Certain kinds of blown oils tend to be more compatible than raw oils.

### INDUSTRIAL USES

Very satisfactory metal lacquers can be formulated from these products, which materials are durable as clear outdoor lacquers on metals, such as brass, copper, aluminum, and its alloys, cold-rolled steel, etc. Recommended formulas for such lacquers employ resins such as Rezyl 14,† dammar, and Vinsol (the latter is very dark in color).

A typical formulation for metal is:

\* Compatible in the presence of 1- and 2-nitropropane.

† Manufactured by American Cyanamid Company.

C. A. butyrate or propionate .....	5.0% by wt.
Rezyl 14 Sol. (50% 1:1 Bu. Ac.-Tol.) .....	2.5%
Dibutyl phthalate .....	2.1%
Acetone .....	10.0%
Ethylene dichloride .....	23.3%
Toluene .....	21.1%
Ethyl lactate .....	3.3%
Butanol .....	2.0%
Ethyl acetate .....	20.0%
Methyl propyl ketone .....	10.7%

100.0%

In making a solution of these plastics, it is desirable to reverse the usual process of dissolving nitrocellulose. The customary practice is to wet the cotton with non-solvents first and then bring it into solution with active solvents. These plastics are better cut in active solvents, only, or a mixture of the active solvents, with the remainder of the solvents formula added to the base solution. A typical solvent formula is:

SPRAYING		BRUSHING	
Acetone .....	42	Acetone .....	27.0
Ethylene dichloride .....	30	Ethyl acetate .....	13.5
Butanol .....	3	Butanol .....	4.1
Methyl ethyl ketone .....	15	Methyl Cellosolve acetate .....	16.9
Methyl Cellosolve acetate .....	10	Ethyl lactate .....	16.9
		Toluene .....	21.6

## DIPPING

Ethyl acetate .....	35
Ethylene dichloride .....	50
Butanol .....	5
Ethyl lactate .....	10

These suggested solvent combinations are rich in high-boiling solvents, and may be made less expensive by the further addition of low-boiling solvents and diluents, except where a very unusual condition is met with. In general, cellulose acetate butyrate of high butyryl content, such as C.A.B., Type II, has a greater range of solubility than either cellulose acetate butyrate, C.A.B., Type I, or cellulose acetate propionate, C.A.P., Type I, which in turn have better solubility than cellulose acetate butyrate of low butyryl content, such as C.A.B., Type I.

Lacquers made from these products possess excellent resistance to light discoloration and are recommended for use where such a finish is desired. Their stability from heat decomposition is excellent and automatically suggests their use in high heat-resisting finishes.

Recent investigation (4) disclosed the fact that cellulose acetate butyrate is an ideal product for airplane dopes and imparts excellent tautness and non-shrinking qualities in humid weather, in addition to non-flammability and resistance to gasoline.

It is believed that with further improvement in manufacturing processes, and the variation of the ratios of butyryl-propionyl-acetyl groups, together with modification of the hydroxyl content of these mixed esters, new useful products will be available for the lacquer industry.

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## PRINTING INKS





## CHAPTER 21

### PRINTING INKS

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SCHLEICHER, and JOSEPH J. MATTIELLO

#### FUNDAMENTALS OF PRINTING INKS

Printing inks, in their simplest form, are fine dispersions of pigments and/or solutions of dyes in vehicles capable of imparting the properties peculiar to their respective printing process. These dispersions or inks are distributed in a thin film by the printing press to the printing plate and are reproduced by pressure contact on the surface of the material (paper, cloth, metal, etc.) being printed. The thin films become dry and hard by various means, depending on their formulation and the printing surface.

The fundamentals of ink making in use centuries ago are employed today with modern revisions. The modern trend leans toward better dispersion, improved pigments, and improved vehicles through the use of synthetic resins and oils. The factors governing ink manufacturing are type and speed of press, time of drying, and type of material being printed. Technical control and greater employment of the research chemist resulted in developments of new types of inks which were only printers' dreams a few years ago.

Since the art of printing is divided into three main classes, namely, relief or letterpress, intaglio, and planographic, it perforce follows that printing inks also take the same classification. Necessarily, however, since each of these methods of printing embraces in itself widely varied applications, a different type of printing ink is needed for each.

#### General Properties

**Relief or letterpress inks** include those made for platen or job presses, for flat bed or cylinder presses, for rotary presses, which include both newspaper and magazine printing presses, and for dry offset presses. Generally speaking, letterpress inks dry by any of the

following methods: simple penetration, penetration and oxidation, oxidation and forced evaporation. These different types of inks are discussed later under their respective headings.

In relief or letterpress the consistency varies from highly fluid for news inks to the stiff pasty consistency for bookbinders' inks as used for printing cloth book covers. News ink is used on high-speed presses and dries by penetration in the paper fiber of the highly absorbent newsprint paper. Other types of relief or letterpress inks for cylinder, job, bond, and bookbinders' inks are of a heavier consistency than news inks. The cylinder type presses do not exert as much pressure at the moment of impact on the printing material as do the job or platen presses. These inks dry mainly by oxidation with some penetration. The penetration generally increases with decreased viscosity, but this is also governed by the type of vehicle used and whether the material being printed is absorbent or non-absorbent.

Halftone process inks are formulated with pigments of fine particle size and easy grinding characteristics. These inks must be ground extremely fine to insure sharp printing of the halftone screen. If not, the ink will gradually fill up the spaces between the dots and soon print a flat solid.

**Intaglio inks** include those made for rotogravure, steel engravings, copper plate engravings, and to a minor extent etching inks.

Intaglio inks are manufactured with a very fluid consistency. This is necessary so that the scraper blade on the rotary press will remove all the excess ink from the image in the copper cylinder, and so that the proper quantity of ink for the impression is retained. Soft pigments must be resorted to so that the copper cylinder will not be scratched when the ink gathers under the scraper blade. In flat-plate gravure printing the excess ink is wiped off with cloth and must, therefore, be pasty rather than viscous. Sulfur colors must be avoided because of the formation of copper sulfide on the cylinder. Sulfide formation can be avoided by chromium plating the copper cylinder. The vehicle used in these inks is a solution of resins, natural or synthetic, in volatile solvents and dries mainly by evaporation.

**Planographic (lithographic or offset) inks** include those made for regular lithography and offset presses.

Lithographic or offset inks are manufactured with a heavier body (consistency) than letterpress inks. They have a maximum pigment concentration and use a more viscous vehicle, both being necessary for the printing process employed.

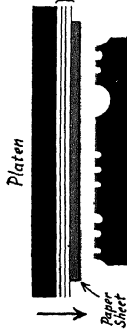
# PRINTING METHODS

Drawings by OTTO W. TURNERMAN

## RELIEF (TYPOGRAPHIC)

### FLAT-BED

#### Hand and Platen Press

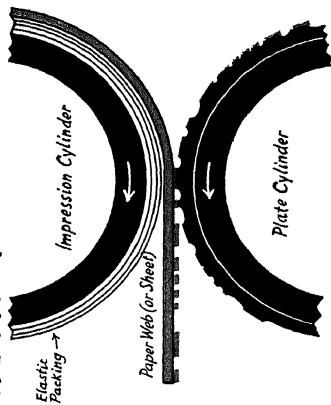


*Paper showing indentions on back*



*Paper showing indentions on back*

### ROTARY

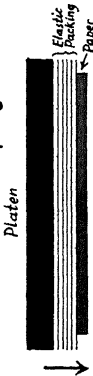


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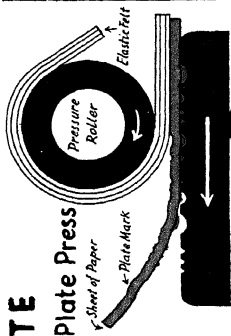
# GRAVURE (INTAGLIO)

## FLAT-PLATE

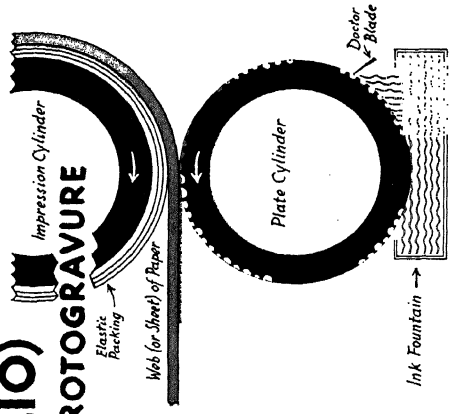
### Steel Die Stamping



### Plate Press



## ROTOGRAVURE



*Paper showing reverse indentations on back, on Flat-Plate work*

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The diagrams are meant to show, at a glance, the relation of ink (red), paper (blue), printing plates, and printing machinery in the three main groups of printing methods.

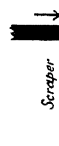
While differentiation in thickness of blocks and plates, and

in curvature of cylinders is shown, none of the dimensions may be taken as actual. The thickness of paper, plates, and film of ink, and the size of halftone dots had to be exaggerated for the sake of clarity.

# PLANOGRAPHIC

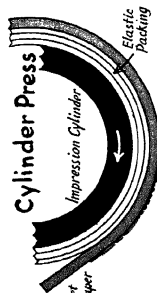
## FLAT-BED

### Hand Press



Scrapper

Sheet of Paper

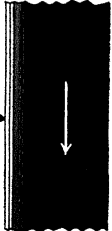


Cylinder Press

Elastic Packing



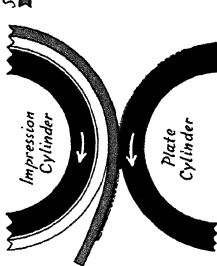
Paper showing no indentions on back



Paper showing no indentions on back

## ROTARY

### Direct

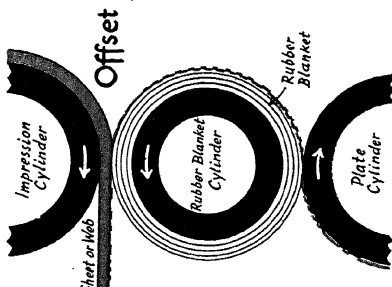


Impression Cylinder

Plate Cylinder

Paper showing no indentions on back

### Offset



Impression Cylinder

Sheet or Web

Rubber Blanket Cylinder

Plate Cylinder

## RELIEF

**Hand and Platen Press.** Type or block (wood, linoleum, electrotype, stereotype) inked on relief surface; paper pressed against form all at once; size of sheet and press limited, because of pressure required.

**Cylinder Press.** Printing form same as before; use of rolling pressure (cylinder) makes printing of large sheets possible;

pressure is exerted at the tangential line of contact. Bed with form moves back and forth.

**Rotary Press.** Printing form (electrotype or stereotype) curved around a cylinder which is in mesh with impression cylinder, both spinning continuously.

In all cases a moderately elastic packing on the pressing surface insures a clean transfer of ink to paper, the printed

lines showing a slight indentation on the back of the paper. The best printing shows the ink glossy.

### GRAVURE

**Steel Die Stamping.** Solid metal plate has the lines of the work engraved into it; the resulting grooves are filled with stiff ink; the polished top is wiped so that ink remains only in the recesses. Heavy pressure, with elastic packing, forces the paper into the recesses, and upon release the paper lifts out the ink. The paper shows reverse indentation on the back and corresponding relief on the front. Sheets limited to small size.

**Plate Press.** Solid metal plate is inked and wiped, as before. Heavy, elastic pressure is applied by two metal rollers. The printed sheet shows a blind impression of the plate edge, all around the work; also reverse indentation on back, and the ink in noticeable relief.

In both cases the pressure rests primarily on the ink-free surface (non-printing). The ink shows a velvety depth (non-glossy).

**Rotogravure.** The work is etched on a copper cylinder, in the form of recessed cells of uniform spacing but of varying depth (created by the halftone screen). The plate cylinder dips into a trough filled with ink thinned with a quickly evaporating solvent, and is scraped clean by the Doctor Blade. The varying quantity of ink left in the cells (of varying depth)

produces lighter or darker dots, corresponding to the tone values of the picture. Line work (type) shows the criss-cross screen pattern.

### PLANOGRAPHIC

**Hand Press.** Lithographic stone or metal plate has the work prepared chemically on a level surface, so that it will be ink-receptive and water-repelling, while the non-printing background is kept moist and thus ink-repelling. Printing is done by a scraping action, with elastic interlay.

**Cylinder Press.** Stone or plate is prepared the same as before; the cylinder exerts a rolling pressure; elastic packing is needed as the whole surface (whether printing or not) is under pressure at the tangential line. Press bed moves back and forth.

**Rotary Press.** A chemically prepared thin metal plate clamped around a cylinder insures speedy printing.

In the preceding three cases full surfaces can be printed with a full flow of ink; no indentations show on back of paper. Ink is rich in pigment and normally without gloss.

**Offset.** The ink on the plate cylinder is transferred to a rubber-blanketed cylinder and then in turn onto the paper led around the impression cylinder. The elasticity of the rubber blanket insures printing of delicate detail (halftone screen) even on rough paper, but the quantity of ink on full surfaces transferred by the rubber is limited; hence the ink appears flat (gray), in contrast with relief or gravure printing.

### General Remarks

The pigments used in the ink industry may be grouped in the same order as for the paint maker. (See Chapter 1, Volume II.)

The important characteristics of pigments for the ink industry are maximum color strength, cleanliness, small particle size, ease of grinding, permanence or fastness to light, chemical inertness, non-bleeding in oils, solvents or water and transparency or opacity. Concentrated colors are particularly desirable in formulating an ink as a concentrated ink enables the printer to run a minimum film of ink, thereby eliminating the difficulties of "offset," i.e., partial transfer of freshly printed ink to the under side of sheets assembled in a pile, as they come off the press.

Cheapest and largest in volume of the printing vehicles are the news ink varnishes. These are composed of petroleum (mineral) oils with or without rosin, or other resins with the gilsonite added to increase viscosity, length, and dispersion. The vehicle of next importance is heat-bodied linseed oil (lithographic varnish), and, following this, are the heat-bodied perilla, tung (China wood), oiticica, and dehydrated castor oil varnishes. Another important vehicle is rosin varnish, which is a blend of rosin with rosin oil or mineral oils. This is used alone or in combination with the other vehicles mentioned.

The technique of ink making consists very largely of detail. Vehicles and pigments must be blended to obtain the required balance for proper viscosity, flow, tack, and penetration on a large variety of printing presses, paper stocks, and printing surfaces. The different inks will dry to a solid film differently, depending upon their use, surfaces employed, and their composition. News inks dry mainly by penetration and absorption; aniline inks dry by evaporation; lithographic inks dry mainly by oxidation with some polymerization if air-dried; and template inks dry mainly by polymerization with some oxidation. These latter inks are baked to a hard film.

### HISTORY OF PRINTING INKS

There are vague references to printing by the woodblock method, for the purpose of textile decoration, in Chinese records as far back as the reign of Wu Wang, about 1200 B.C. The stamping of blocks containing lettering upon silk and other materials, with a gummy, water-soluble writing fluid, is, no doubt, a very old technique and was practiced many centuries before the Christian era.



Printing, as a method of reproduction, can be spoken of only in connection with paper. This material was first made in A.D. 105, according to a report in old Chinese Annals recently come to light (5). Although primarily a material for writing, paper became useful as a means of duplicating and multiplying designs and characters carved in relief in a plane slab of wood. Thus "the block printing" of pictures and texts began.

All references to Oriental printing must be understood to be block stamping or rubbing, the "ink" being the customary Chinese black or sepia writing fluid, applied by pad or brush to the surface of the wood block. For "printing" the paper was laid on the inked block and rubbed on the back, no press being required. This method of "printing," still practiced today, together with paper and its manufacture, was brought to Europe through the channels of trade by the Islamic people.

The Moors set up the first papermill in Europe at Xativa, Spain, in 1150; the first mill in Italy was built in Montefano, Umbria, in 1276. From then on the manufacture extended into France (Herault, 1189), Germany (Nuremberg, 1391), the Low Countries, and, finally, England (Hertford, 1494). The first papermill in the American colonies was erected by Rittenhouse and Bradford in Germantown, Philadelphia, in 1690.

The earliest extant pieces of "printing" are Buddhistic prayer slips, during the reign of the empress Shotoku, A.D. 770.

The earliest block-printed book is the "Diamond Sutra" of 868, found by Sir Aurel Stein, and now in the British Museum (5). It is likely that other books were printed before, but they have not survived.

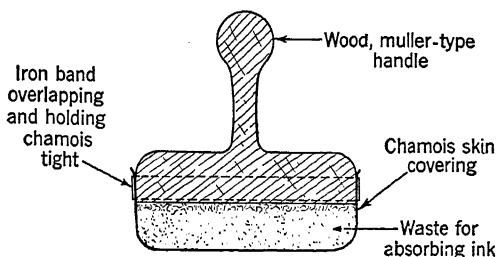
Great quantities of books were produced by woodblock printing over a period of nearly a thousand years, while the Chinese Empire flourished, some of the official editions of the Classics, the laws, and encyclopedic texts running to 200 to 300 volumes at times (5). These are truly staggering figures.

In Europe printing from movable type is credited to Gutenberg, who set up his press in Mainz in 1445. The cast metal types could not be printed with gummy, water-soluble ink, theretofore used in woodblock printing. Gutenberg was the first to use linseed oil varnish, with lampblack as a pigment—the ideal printing ink up to this very day.

The early printer saturated a pad with the ink, placed the pad on a holder with handle, and fastened over the pad a lintless cloth or porous animal tissue held in place by an iron band. The type face was then patted or rubbed so that the ink lay on the type.

The ink made by German printers was an excellent rich black. The varnish was first made by boiling raw linseed oil in an open iron kettle, over a wood fire, until the desired tack and body were obtained. This was mixed and mulled with a black pigment made by burning oils. The soot from the burning oil was deposited on a cool metal surface, from which it was scraped and collected as a black pigment. This was the method used by earlier portrait painters who made their own paints.

The Venetian Canneparius in *De Atramentis* (4) wrote of printing ink consisting of one pound of a varnish of linseed oil and juniper



Known as "Ink Pad" or "Dabber" or "Printers' Ball." The last is the common term of the trade.

gum, thoroughly incorporated with one ounce of smoke black and boiled over a slow fire to the desired consistency. Moxon (16) in his *Mechanick Exercises*, in 1683, mentioned printing ink in England as being inferior to the Dutch ink. This was because the Dutch used only a small quantity of rosin (one-half to one pound to the gallon) whereas the English used a greater amount of rosin with the linseed oil, and often used fish oil as an adulterant, which caused excessive bleeding of the oil through the paper.

Fertel, a French printer (9) in St. Omer in 1723, wrote on the manufacture of printing ink with turpentine. The black was made from burning pitch resin, in open pots, the smoke going into a collecting chamber hung with sheepskins to collect the black. This black was mixed with varnish (five ounces to two pounds). Savage (21) stated that the proportion of black was too small for good ink.

In 1751, Breton (2) wrote of a printing ink made by heating 110 pounds of nut oil for two hours in a vessel, then burning several times, and reheating for three hours until it had the consistency of glue. This was strained and yielded 100 pounds of varnish, which was incorporated with lampblack (two and one-half ounces to one pound).

Litharge used by many was condemned by Breton, Mitchell, Savage, and others (2, 15, and 21) as clogging the type.

The *Encyclopædia Britannica*, 1823, described litharge and its use to aid drying and the addition of soap to overcome the clogging of the type.

The early colonial printers of the United States imported their inks from England and Europe. Printing started in the United States in Cambridge, Massachusetts, in 1640. Other early American printers were Roger and Fowle of Boston, about 1750.

### RAW MATERIAL CHART AND FLOW SHEET

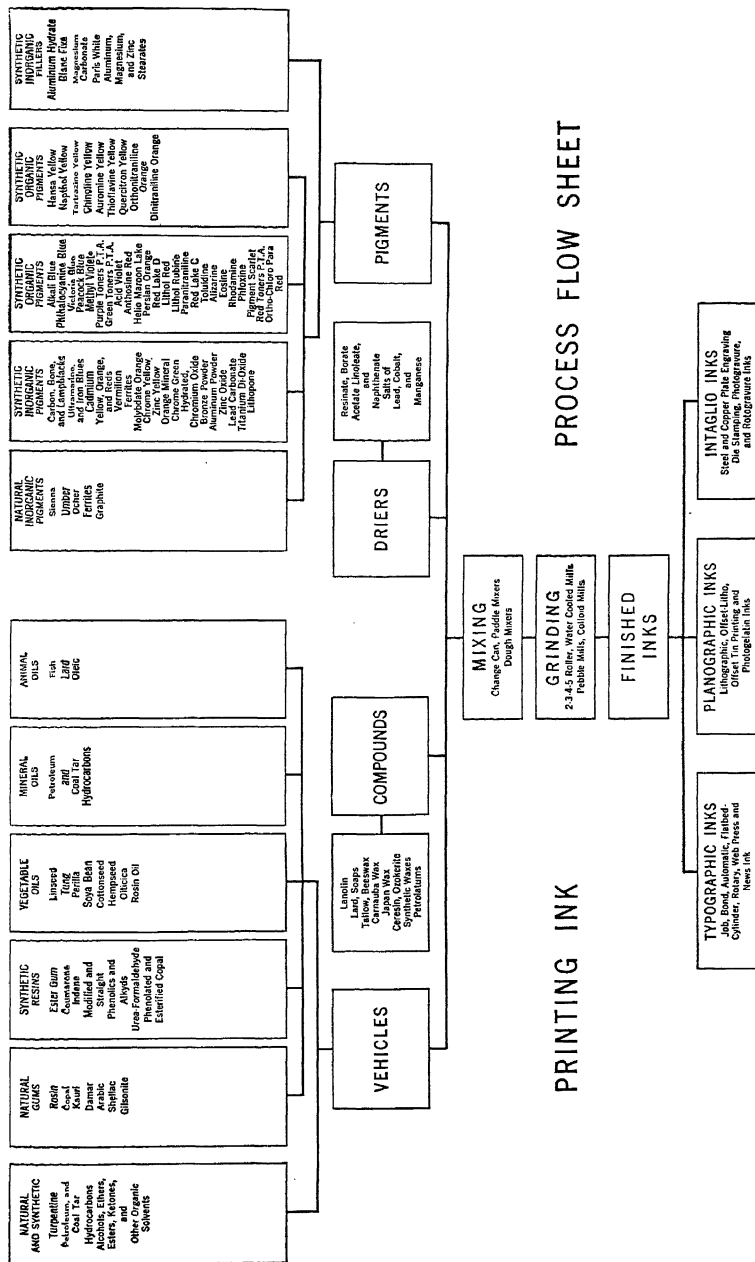
Figure 1 shows diagrammatically the raw materials, composition, general methods of manufacturing, and types of inks mainly used in the ink industry.

### INK VEHICLES

The working qualities (meaning ease of spreading ink into thin films), printability, and finish of an ink film depend upon the use of proper equipment, the paper, and the specific formulation of the ink. It has been mentioned that inks are generally composed of pigments, vehicles, driers, compounds, and waxes. To get the best printing results, the inks must have the heaviest consistency that the speed of the press and the surface of the material being printed will permit. This consistency is controlled largely by the viscosity of the vehicle and by the ratio of pigment to vehicle. The most important characteristics of a vehicle which govern the consistency of an ink are viscosity, shortness, wettability, flow, length, and tack. These characteristics are governed by the viscosity of the vehicle and depend upon the ratio of the various ingredients, such as resin-to-oil or resin-to-oil-to-compound-to-thinners, and also upon the method of processing.

The number and kind of vehicles used by the ink industry are, at present, as varied as those employed in the paints, varnishes, and lacquers. The vehicles employed in the ink industry may be composed as follows:

1. One or several heat-processed vegetable oils.
2. Menhaden fish oil alone, or heat-processed in combination with vegetable oils.
3. Vegetable oils in combination with resins, driers, with or without volatile thinner and waxes.



4. Petroleum oils (mineral oils) of high and low fractions, with or without resins.
5. Resin with plasticizer and a volatile thinner.
6. Cellulose esters, plasticizer, and low- or high-boiling solvent.
7. Casein water emulsion.
8. Sharply thermoplastic compounds.

The most important characteristic of a vehicle is its binding property for the pigments and its ability to fix the ink film firmly on the printing surface.

### Functions of Constituents

Before entering into a general discussion of the uses of specific vehicles, the general function exhibited by each of the main constituents employed in making a general vehicle will be described. The vehicles may be divided according to use into oleoresinous, lacquer, spirit, and miscellaneous vehicles.

### Oleoresinous Types of Vehicles

These vehicles, commonly known as varnishes, are composed mainly of drying oils, resins, driers, compounds or waxes, and sometimes thinners and/or anti-oxidant. Each of these constituents functions as follows:

1. The oils supply the elements of oxidation (for drying), elasticity, toughness, adhesion, durability, and tack.
2. The resins provide the elements of hardness, resistance to wear, waterproofness, acid and alkali resistance. They also impart tack, gloss, and, in some instances, may assist in drying.
3. The driers accelerate (shorten) the time of drying. The most effective driers are cobalt, manganese, lead, and zinc.
4. The thinners are used to reduce the viscosity or consistency and tack in order to develop easy working of the vehicle, which property is also imparted to the finished ink. Thinner will also increase penetration, and thereby aid adhesion to paper stock. As a result of these properties they have a tendency to minimize offset.
5. The waxes and compounds impart shortness, thereby introduce setting of ink, reduce tack, and minimize offset.
6. Anti-oxidants have the property of retarding oxidation and thereby retard the drying of the ink film; sometimes desirable.

Some of the vehicles are composed only of linseed oil in a viscous (bodied) state; they are known as lithographic varnishes. Other vehicles are composed of several drying oils, and still others of resins and volatile thinner.

All of these vehicles are used for making letterpress, lithographic and offset, and gravure or intaglio inks.

### Spirit Vehicles

Generally speaking, these vehicles should include all those composed of resins and volatile thinners. Specifically, however, only those composed of shellac or Manila resins, with alcohol as thinners, are spoken of as spirit vehicles or varnishes. They are used in aniline inks. Some of the vehicles which are made only of a synthetic resin and petroleum and other hydrocarbon thinners are used for heat-set inks.

### Nitrocellulose Vehicles

These vehicles, commonly known as lacquers, are composed mainly of nitrocellulose, resin, plasticizer, solvents, and diluents. Each of these constituents functions as follows:

1. Nitrocellulose (pyroxylin) provides the element of toughness and hardness and causes rapid formation of dried film. Viscosity of the vehicle is controlled by the use of the  $\frac{1}{2}$ -second to 5-second and heavier viscosity nitrocellulose. Greater detail on this phase can be obtained by referring to Chapter 18.
2. The resins impart adhesion, gloss, and hardness, and some resins impart plasticizing properties.
3. The plasticizers impart the elements of elasticity, durability, and adhesion.
4. The solvents and diluents have the important function of solvency and reducing viscosity or consistency to permit easy spreading of ink films.

These vehicles are used mainly in rotogravure ink and other quick-drying inks.

### Vegetable Oils

We shall first consider the vegetable oils because at present the larger proportion of the vehicles employed in the printing ink industry are composed mainly of vegetable oils. The oils are divided into *dry-*

*ing oils*, such as linseed, perilla, tung, and oiticica; *semi-drying oils*, such as soybean, walnut, sunflower, hempseed, corn, and cottonseed; and *non-drying oils*, such as castor oil.

The first two classes of oils will dry under normal atmospheric conditions to a fairly hard and elastic film, mainly by oxidation. The drying vegetable oils require less oxygen and time to air-dry to a hard film than the semi-drying oils. The iodine number is generally used for the classification of the oils (exception: tung, oiticica, and dehydrated oils) into their respective class. The iodine number of the drying oils will vary from 210 to 165; for the semi-drying oils from 158 to 120.

All the oils whose iodine number is less than 120 are considered non-drying oils.

These oils are discussed in greater detail in the chapters on oils (Chapters 1 to 6, Volume I).

### Drying Oils

**Linseed oil** is of prime importance as it constitutes over 75 per cent of the oil used in this industry.

Raw linseed oil has a golden yellow color and a pleasant odor, and its iodine number varies from 175 to 180.

The alkali-refined and the slightly blown linseed oils are largely used in the making of ink vehicles. Both these are used in the making of lithographic "litho" varnishes; the former for making the transparent or pale, and the latter for the dark (amber) colored varnishes.

**Lithographic varnishes** are heat-bodied linseed oils, whose viscosity has been increased by heat processing the raw oil. In the history of the development of printing ink manufacture, it was known, at an early date, that raw oils, particularly linseed oil, were too greasy and would not be satisfactory for the manufacture of inks. Moxon, 1683 (16), mentions this fact, as does Savage, 1822, who refers to Moxon's observations. It was found that linseed oil had to be bodied to make a satisfactory ink, that is increased in viscosity to eliminate the greasy characteristics. This was done by heating the oils in an open kettle, the criterion of heat being judged by whether a slice of bread charred or not. Unadulterated linseed oil was bodied by the Germans and Dutch until a string corresponding to a No. 1 lithographic varnish (see Table I) was obtained, usually an all day cook—8 to 10 hours.

The lithographic varnishes, the regular or amber, and the transparent or pale colors are regularly made in twelve different viscosities (called "body" in the ink industry), which vary from approximately

0.65 to 150 poises. Like the paint industry, the ink industry was also a development of the arts. Wolfe (27) also stated that the twelve different viscosities of the lithographic varnishes were not chosen by any scientific reasoning, but rather by a development of the arts. In the United States a definite nomenclature has grown up to identify the lithographic varnishes. The varnish of the thinnest "body" or lowest in viscosity is called five naught "litho"; and the heaviest in "body" or highest in viscosity is called eight "litho." The naught numbers are used for the lower viscosity varnishes; the cardinal numbers are used for the heavier viscosity varnishes. For convenience in discussing the complete range of the lithographic varnishes and their uses in inks, they will be divided into four groups—the "thin," the "medium," the "heavy," and the "very heavy bodied" varnishes, as shown in Table I. This table will also indicate the viscosity in approximate poises for each "body," the specific gravity at 60° F. (15.6° C.) and the approximate weight in U. S. gallons.

TABLE I

## LITHOGRAPHIC VARNISHES

(Body, or consistency, viscosity in poises, specific gravity, and weight per gallon)

	"Body" Name Used in Industry	Viscosity Poises * Approximate	Specific Gravity at 60° F. 15.5° C.	Approx. Weight per U. S. Gallon
Thin-bodied	00000	2.08	0.946	7.8
	0000	2.90	0.949	7.9
	000	4.34	0.957	8.0
Medium-bodied	00	10.30	0.961	8.0
	0	14.60	0.964	8.0
	1	26.00	0.968	8.0
	2	32.80	0.971	8.0
Heavy-bodied	3	56.60	0.974	8.1
	4	74.30	0.975	8.1
	5	137.00	0.977	8.1
Very heavy-bodied	7		0.987	8.2
	8		0.996	8.3

\* The approximate viscosity of raw linseed oil is 0.50 poise.



This table represents the range in viscosity as used by several of the well-established varnish manufacturers who have supplied the ink industry for many years. The viscosity for each "body" as made by other varnish manufacturers may vary slightly or greatly from the values given in the table. The ink industry should establish a standard range of allowable viscosity for each body.

*Manufacturing Lithographic Varnishes.* Lithographic varnishes are heat-bodied in iron, copper, aluminum, stainless, or Monel kettles, varying in size from 25 to 800 gallons. A sixty-gallon kettle is the standard for a fifty-gallon batch. These kettles are usually cylindrical in type, with upper surface opened to the atmosphere. Recently, several closed systems of heat-bodying the varnish have been introduced in our industry. In these systems, the varnishes may be processed in a vacuum or in an atmosphere of carbon dioxide. There are two systems of processing the varnishes in an atmosphere of carbon dioxide gas: in one system the gas is bubbled from the bottom of the kettle, pulling along whatever decomposition products it can under its own pressure; and in the other, the gas acts only as a blanket. In this latter system, a partial vacuum also exists. These systems and others are discussed in detail in Chapter 3.

The aluminum, stainless steel, and Monel kettles yield pale varnishes; the copper and iron kettles produce darker varnishes because small amounts of the metallic copper and iron will dissolve in the hot varnish. Some kettles used are lined with porcelain enamel, and they give very pale varnishes.

The time required to heat-process these varnishes varies from several hours to approximately twenty-four hours, depending upon the "body" or viscosity wanted, the top processing temperatures, and the size of the batch. The charge of kettle, which is usually about two-thirds full, is slowly heated to temperatures varying from 525 to 625° F. (273.9 to 329.5° C.).

With the information and data as developed to date, it is rather difficult to know the exact chemical composition of lithographic varnishes. During the processing of heat-bodying the oil from its raw state to that of a heavy viscous liquid, many changes, both physical and chemical, take place concurrently. However, it is agreed that the reaction of polymerization takes place to a greater extent than all the other reactions together, such as rearrangement, hydrolysis, cracking, oxidation, and condensation. It is the reaction of polymerization that is mainly responsible for the increase in viscosity. The trend of changes of all the various measurable physical and

chemical characteristics during processing are discussed in Chapter 3. Also see Chapter 4.

However, for the purpose of this chapter, it should be stated that a lithographic varnish is composed of several phases, each of a different viscosity, varying from a liquid phase progressively to a gel phase. The more viscous phase is dispersed in the less viscous one.

In a "thin-bodied" varnish, there is present a negligible quantity of the gel phase; in a "heavy" or a "very heavy-bodied" varnish, the gel phase predominates. If a condition exists where the so-called liquid phases are insufficient to disperse the gel phases, a solid gel is obtained. This partial explanation of a bodied varnish will help to explain why lithographic varnishes of several viscosities are used in the formulation of inks.

It has been stated earlier that the important properties of the vehicles (varnishes) are shortness, viscosity, wettability, flow, length,\* and tack.

A knowledge of the predominant properties exhibited by each group of the lithographic varnishes is very useful to the ink formulator, because these properties of the varnishes are also exhibited, to a large extent, by the inks in which they are used.

In the formulation of a letterpress, lithographic, gravure, or intaglio ink for plate work, or an offset ink, several varnishes of different body (viscosity) are generally employed, i.e., the thin-bodied varnish for shortness or softness; the "medium-bodied" varnish for wetting, flow, and length; and the "heavy" and "very heavy-bodied" varnishes for tack and for increasing the binding property of the total vehicle for the pigments.

The consistency of a finished ink is largely controlled by the viscosity of the varnishes employed.

*The thin-bodied lithographic varnishes* exhibit mainly the property of shortness, which is associated with the poor wetting of the varnishes for pigments. As the varnishes of this group increase in viscosity from No. 00000 to No. 000, the shortness becomes less, while the wetting increases. They also penetrate into paper stock considerably more than the heavier-bodied varnishes, thereby removing from the ink a portion of the vehicle generally needed as a binder for the pig-

\* The length or shortness of a varnish is measured by the length of a string formed by the pigment-oil paste, or the bodied oil alone at the breaking point. A very short varnish will give a practically zero-length string; the long varnish may produce a string from one-quarter to several inches in length. See also *Bulletin 192*, Dept. of Interior, Bureau of Mines.

ments. These varnishes have limited tack and thus cause poor distribution of the ink on the press roll, plate, type, or paper. The very small amount of tack, usually associated with these varnishes, is due to the presence of only a very small quantity of gel phase. These varnishes emulsify more easily than the heavier ones with the damping solutions always used in lithographic printing, thus causing poor reproduction or definition in printing.

However, because of their relatively poor wetting, these vehicles impart a partial buttery (shortness) consistency to the ink in which they are used. They do aid in setting the ink in the paper stock.

*The medium-bodied lithographic varnishes* are considered to have good wettability, good flow, and good length. They also exhibit a certain amount of tack. Because of these properties, these varnishes are very good grinding mediums for pigments. They penetrate considerably less than the thin-bodied varnishes, permitting most of the vehicle to remain on the top of the paper, and, in this way, act as a good binder for the pigments of the ink film. The amount of tack exhibited by these vehicles permits good distribution of the ink on the press rollers, plates, type, and paper. These are the most commonly used varnishes.

*The heavy and very heavy-bodied lithographic varnishes* are considered to have mainly tack, a characteristic which permits sharp printability. These varnishes have very good binding properties for the pigments, owing to their excellent cohesive forces. The presence of a small amount of these varnishes in an ink prevents it from emulsifying with the damping solutions used in lithography, thereby giving good and sharp printability.

The high tack property of these varnishes is due to the presence of a very large quantity of the gel phase. Because of this high tack property, only small quantities are used since large amounts will develop too much tack in an ink and thereby cause "offsetting"\* and picking.†

The proportions of the different lithographic varnishes to be used usually depend upon the consistency of the ink desired; and this in turn is guided by the:

1. Speed of the press.
2. Design of press and inking facilities.

\* Offsetting is the transfer of ink from the print to the underside of the sheet above in the pile of stock collected from the press after printing.

† Picking is the rupture of the coating or the fibers of the stock itself which imparts foreign particles to the ink and produces spotted print.

3. Method of printing.
4. Size or type of form.
5. Stock (surface to be printed).

**Livering** is one of the most common problems of the printing ink industry as well as the paint industry. It is a term applied to a state of fixed rigidity of a pigment-oil paste, resulting from a drastic change in consistency upon standing. This phenomenon of livering is discussed in detail in Chapter 4, Vol. IV.

**Burnt or Plate Oil.** In printing from a plate on which the design is engraved or recessed, the ink is held in the hollows while the surface of the plate is wiped clean. The "litho" (lithographic varnishes) oils are too greasy. Satisfactory oils which can be wiped clean off the plate or surface have been obtained by burning the oil. The linseed oil is heat-bodied to approximately 475° F. (246.1° C.) and then the exposed surface is set on fire. This is kept under control for 2 to 5 hours, until an oil of the proper viscosity is obtained. In Table II a comparison is given between the "body" or viscosity of the plate oils versus the lithographic varnishes of Table I.

TABLE II

"Body" OR VISCOSITY COMPARISON

vs.

"Body" of Plate Oil	Lithographic Varnishes
0½	0000
1	000
2	00
2½	0
3	1
4	2
5	3

For approximate values of the viscosity in poises and specific gravity, see Table I.

**Tung or China wood oil**, within the last thirty years, has found a definite place in the ink industry. The oil is pressed from the nut of the tree, which grows mainly in China. It dries faster and has decidedly better alkali resistance than linseed and perilla oils.

Tung oil in the raw state when dried gives a frosted film, but when properly heat-treated it gives a lustrous, tough, flexible film. In addition, because of its quick drying, and good water and alkali resistance, the tung oil is used in the making of quicker-drying inks, soap wrap-

per inks, overprint varnishes, and gloss inks. It is also used to a great extent in vehicles for metallic inks.

**Oiticica oil**, a nut oil, is a native product of the northern part of Brazil. It resembles tung oil in many of its chemical and practical properties. It dries more slowly than tung oil, but more rapidly than linseed and perilla. The water resistance of oiticica oil is generally considered better than linseed and perilla but poorer than tung oil. This oil is used mainly in the bodied state and is employed only as a partial substitute for tung oil.

**Dehydrated castor oil** is a chemically manufactured oil produced from castor oil. It is chemically and practically similar to tung oil in many respects, and is used as a partial substitute for tung oil.

### **Semi-Drying Vegetable Oils**

**Soybean oil** dries much more slowly than linseed oil. Because of its very slow drying, it can be used only to a limited extent in the ink industry. It can be bodied similarly to linseed oil but requires considerably more heating time. This oil has been used in mixture with perilla to get a combination that dries in a way similar to linseed oil. Whereas the apparent drying appears to be similar to linseed, the final thorough drying is poor. It discolors less than the faster-drying oils and menhaden fish oil.

The greasy properties of the soybean oil make it unsuitable for use in offset or lithographic inks and in plate and engraving inks.

There are other semi-drying oils, such as hempseed, poppy seed, sunflower seed, tobacco seed, and walnut oils. Their use in the ink industry is very limited because of their semi-drying characteristics.

### **Resins in Inks**

The natural resins were the first to be employed in ink vehicles; they were used to develop:

1. Good adhesion in an ink.
2. Sharp and clean printing.

In modern printing, in addition to the properties already mentioned, the synthetic resins are employed to produce:

1. Speed in drying.
2. Hardness and toughness or scratchproof (mar resistance).
3. High gloss.

Until recently, the natural resins, such as rosin-limed and congo, were the chief ones employed. These resins were later replaced largely by ester gum, which was the first synthetic resin to be used by the ink industry. Today, the entire general field of synthetic resins has invaded the ink industry, and they may be classified into eight general types:

1. Ester gum.
2. Rosin-modified phenolic.
3. Rosin-modified maleic.
4. Ester gum-modified phenolics.
5. 100 per cent phenolic.
6. Coumarone-indene.
7. Alkyd.
8. Urea-formaldehyde.

These resins are discussed in detail in Chapters 10, 12, 13, 14, 15, and 16, Volume I.

The most important property of modern printing—"speed of drying"—has been largely responsible for the increased use of resins and the introduction of gloss inks, which require greater amounts of resins, in ink vehicles.

The type of drying required of an ink largely influences the choice of resin or resins employed in the ink vehicle. The types of drying usually encountered in printing inks are:

1. Oxidation.
2. Polymerization.
3. Condensation.
4. Penetration and absorption.
5. Evaporation.
6. Solidification.

In many inks, the drying phenomenon frequently consists of a combination of the first three types of drying. In some cases, the drying is controlled by only one type of drying, i.e., news inks dry mainly by penetration and absorption; aniline inks dry by evaporation; tin-plate inks are dried to a hard film by means of heat, and here the drying is due mainly to polymerization and condensation, with some oxidation.

When inks are dried mainly by oxidation, the first six resins mentioned, the ester gum-modified phenolics, 100 per cent phenolic, and

coumarone-indene, are used in combination with drying oils, as the resins themselves have no capacity of oxidation. What drying oil is used depends upon the property desired in the dried ink film, i.e., greater alkali resistance is obtained with the use of tung oil than is obtained with linseed oil.

The amount of resin used in a vehicle (resin-oil combination) depends upon the gloss desired for gloss inks, hardness for scratchproof or non-marring inks, and the viscosity of the vehicle which governs the consistency of the ink.

Modified maleic glyceride resins are used to obtain improved gloss and sharpness of the image.

For highly alkali resistant inks, 100 per cent phenolic resins are employed in combination with tung oil.

A large variety of synthetic resins is used for those vehicles which dry by evaporation of solvents. The properties to consider here are the solubility of resins in solvents, the ease of release of solvents, the residual tack, and thermoplasticity. This last property is important where the heat is used to drive off the solvent. In these vehicles, cellulose esters, ethers, and chlorinated rubber are finding a place.

Alkyd resin vehicles have been used mainly in printing on metal where heat is used to dry the ink. Urea-formaldehyde resins are also being used for this same type of ink.

In many specialized cases, inks may have to withstand the action of acids, alcohols, oils, greases, and other specific chemicals; then the intelligent selection of the resin for the vehicle is important. The inherent resistance to the various chemicals of the vegetable oils and resins is, in turn, largely imparted to a vehicle.

### Driers

Driers used in printing inks are probably the most important and require finer adjustment than any other ingredient. Owing to this fact, they can be troublesome if used incorrectly.

The metals most frequently used in the manufacture of driers are lead, manganese, and cobalt. Each of these metals in the form of metallic salts is used as driers, and they have various effects on drying oils. The effectiveness of a drier is based on the metallic content and its dispersion or solubility in the ink vehicle. Most driers are produced either by a fusion or a precipitation method.

Lead driers are generally used in the form of acetates, linoleates, resinates, or naphthenates. These are the safest driers for use in the first color of process printing, because they have the property of drying

the ink film from the bottom up rather than from the top down, thus presenting a more receptive surface for succeeding colors.

Manganese driers are usually incorporated as borates, linoleates, resinates, or naphthenates. These hasten the drying of ink considerably more than do the corresponding lead driers. Manganese driers have more tendency to dry from the surface. Though not quite as rapid as cobalt drier in this respect, they do dry the ink harder.

Lead acetate and manganese borate driers in combination are used extensively in the manufacture of paste driers. Because of its light color, paste drier is well suited to use in light colors and tints.

Cobalt driers are generally used in the form of acetates, linoleates, resinates, or naphthenates. They are very effective surface driers. Since an ink film is very thin, cobalt drier will dry throughout the film, presenting a very hard surface. In a paint film, which is many times thicker, cobalt drier will only dry the outer surface of the film. Owing to this fact, these driers must be used with caution or the ink will have a tendency to crystallize; in other words, to form a hard non-tacky surface. This would present considerable difficulty, especially in three- or four-color process printing, as an ink will not print properly on the preceding ink if it presents too hard a surface. This surface drying characteristic, however, is an advantage when used in the final color of process printing as it binds all previous colors.

Zinc driers are used to a somewhat limited extent in the ink industry. They are slow-drying catalysts but they also have valuable wetting properties.

The metallic content of driers varies considerably, depending on cost and manufacture. Japan drier generally contains 1.9 per cent lead and 0.6 per cent manganese; paste drier may contain 13.0 to 40.0 per cent lead with 5.5 per cent down to 1.3 per cent manganese; cobalt drier contains 3.0 to 6.0 per cent cobalt.

A combination of driers in an ink has been found to be very effective and often reduces the drying time when compared with the same ink containing only one type of drier. The amounts of driers used in printing inks may vary from 0.1 to 15.0 per cent, this being entirely dependent on the pigment and vehicle used, paper stock or material being printed, type of press, required drying time, and atmospheric conditions. A minimum amount of drier for the required drying time should always be used, as an excessive quantity of drier has been found to retard rather than hasten the drying of an ink film.

. For greater detail on driers see Chapter 22, Volume I.



### Thinners

The thinners employed in inks are of the following type:

1. Normal solvency petroleum.
2. High solvency petroleum.
3. Coal tar solvents.
4. General lacquer solvents for lacquer inks.
5. Chlorinated hydrocarbons.

Of the first type, kerosene has been used to a large extent; and, within recent years, special types with controlled distillation and evaporation rate have been used in heat-set dry inks.

See Chapters 23 to 27, Volume I, for more detailed information.

### Mineral Oils \*

A comparatively short time after petroleum was discovered in Pennsylvania, in the year 1859, certain of its derivatives, in more or less crude form, were employed as compounds and later described as vehicles in the manufacture of news inks. These derivatives were substituted, in part or in whole, for the oils distilled from rosin which were used extensively in this field prior to that time.

With the later discovery of certain types of crude petroleums which yield, under modern methods of petroleum refining, derivatives of particular value to the ink manufacturer, the use of rosin oils in news inks has been virtually eliminated.

According to the proportion of the different types of hydrocarbons present, crude petroleums are classified broadly as "paraffine base" or "naphthene base" or, if intermediate between the two, as "mixed base." Oils are referred to as paraffinic or naphthenic.

In the early use of mineral oil for news ink manufacture, products derived from paraffin base crudes were used, but, since the production of naphthene base crudes (Gulf Coastal Crudes, for example), oils predominantly naphthenic in character have been generally substituted by the ink maker because of their greater suitability for the purpose in question.

Normally, petroleum oils are not easily oxidizable and are therefore included in the group of non-drying oils. Printing inks made with mineral oil vehicles dry by absorption (penetration) into the stock printed upon. This being the case, the oil which is employed should,

\* By A. B. Hoel, pages 630-632.

of necessity, penetrate rapidly and evenly into the paper stock without "showing through" on the surface opposite the printing, thus causing undesirable greasiness and a spotty appearance.

The oil should also be clear and contain a minimum amount of certain colored bodies which have a tendency to stain the paper when absorbed, and cause the paper to take on a gray, yellowish cast. The desirable clear-cut printing is greatly impaired by this stain, which, when encountered, can be overcome to a degree by conditioning the ink with toners, such as methyl violet and other chemicals acting in a similar fashion. These undesirable colored bodies almost invariably occur in low-grade unrefined oils.

It is considered good practice to use clear, wholly distilled mineral oils, free of the stain-producing bodies, in the manufacture of inks. The refinement of the oils must be carried out to such an extent as not only to remove stain-producing compounds but also, at the same time, to maintain within the composition of the oil the types of compounds which have the ability to "wet" the pigment (carbon black for example) and give the proper flow to the finished ink. Oils which wet pigments poorly produce inks of buttery consistency that are of dubious value to the ink maker. In these short inks, the ink maker must resort to compounds which overcome any tendency on the part of the finished ink to gel. These compounds are commonly known as lengthening agents. Refined mineral oils of high naphthenicity have been found to fulfill the above requirements efficiently. They not only are used in the manufacture of news inks but also are to some extent employed in some of the better grades of inks that are indicated for the more or less freely absorbent stocks other than news print.

The naphthenic oils, when used in the manufacture of inks, produce an extremely desirable working ink and, at the same time, impart to it a remarkably lasting plasticizing action. This does not mean that the inked surface is tacky or greasy, but that, in addition to its being dry and non-smudging, it is pliable and not readily chipped or cracked during a normal period of service. With the use of these naphthene oils in litho varnishes, driers are used to a slightly greater degree in inks than in those not plasticized with these mineral oils. In contrast to the suitability of naphthene oils for this purpose, the highly paraffinic types of mineral oils are not so well adapted to this purpose, as it is more difficult to obtain a dry inked surface, free of offsetting, when they are employed in inks.

Some physical data of certain mineral derivatives, which have been customarily used in recent years as constituents of printing ink

vehicles, characterize certain properties which are of prime importance in oils used in these vehicles. Included in these data is the numerical constant denoting the chemical nature of the hydrocarbons, which is commonly known as viscosity-gravity constant or VGC.\* The most paraffinic oils have a VGC of about .80 while the naphthenic oils approximate .90. This constant is therefore a factor of naphthenicity for the oil, and the higher the numerical value, the more naphthenic the oil.

Mineral oils with high VGC's are exceedingly compatible with the several vehicle ingredients used in printing ink compositions, hence finished stable products are obtained. Such oils, when used in news-ink compositions, are quick in wetting the news print and hence render possible the astonishing high-speed printing for which our modern newspaper presses are noted.

### Compounds

"Compounds" are important ingredients of printing inks. They are used to introduce quick setting of the ink into the paper or other stock, to decrease tack, to eliminate picking of the paper surface or coating, to impart shortness to the ink, and to prevent offsetting of the printed film to the underside of the sheet above as they are piled after leaving the press.

The materials used as compounds in printing ink are of a vegetable, animal, and mineral nature. Those most commonly used are lanolin, lard, soaps, tallow, beeswax, carnauba wax, Japan wax, ceresin, ozokerite, petrolatums, and synthetic waxes. They are used separately or in combination, depending on their specific characteristics and the properties desired in a finished ink. Combinations are also made with vegetable oils of the non-drying, semi-drying, and drying types, animal oils, marine oils, distilled or volatile oils, rosin oils, paraffin hydrocarbons, asphaltum, hydrocarbons, and synthetic and natural resins.

\* Viscosity-gravity constants are calculated according to the equation developed by Hill and Coates (*Ind. Eng. Chem.*, **20**, 641 (1928)):

$$\text{VGC} = \frac{10G - 1.0752 \log (V - 38)}{10 - \log (V - 38)}$$

where  $G$  = specific gravity at 60° F.

$V$  = Viscosity in seconds  
(Saybolt Universal at 100° F.)

### Asphaltum

Asphaltum—Natural asphaltums are not used to any great extent in printing ink manufacture. Gilsonite is used to impart toughness, hardness, and aid dispersion in the cheaper grade of black inks.

Cottonseed and stearine pitches are used to impart flow and good wetting qualities. Quite often, combinations of gilsonite, drying oil, and stearine pitch with rosin and mineral oil (sometimes the gilsonite is omitted) are used to make what is known as a flowing varnish. This is added to impart flow to a printing ink.

### Spirit Varnishes

Spirit varnishes are simple solutions of resins in volatile solvents. They dry entirely by evaporation of solvents, and the original resin is left in a thin film holding the pigment.

The copal spirit varnishes, the shellac spirit varnishes, and urea-formaldehyde spirit varnishes are used largely in aniline inks. The composition of these varnishes is described in the section on spirit varnishes in Chapter 8.

The spirit varnishes, composed mainly of maleic and phenolic resins with petroleum thinner, are used in heat-set inks.

## PRINTING INKS

It has been shown that the manufacture of printing ink is generally conducted on the same principle as that of paints. The ingredients used are binding vehicles, pigments, driers, thinners, and compounds of different waxy natures to impart laying and no-offset properties to the finished product.

The machinery used in the manufacture of printing inks is principally change can paddle mixers and dough mixers for thorough mixing of the pigments and vehicles. After this process the grinding is generally done on water-cooled three or five steel roller mills until the pigment is thoroughly dispersed in the vehicles.

### Letterpress Inks

**News inks** are made from cheap petroleum oil, often called black oil because of color, and carbon black. The latter, when mixed in the oil, is then passed through a high-speed roller or a colloid mill. The pigment-vehicle ratio varies with the grades of paper used and type and speed of press. Where less absorbent paper is used, rosin,

gilsonite, and pitch are usually incorporated in the vehicle. When increased color is wanted, more carbon black or lampblack is added with methyl violet or an oil-soluble dye.

**Job printing inks** are formulated to have a medium body (consistency). The vehicle of these inks is generally composed of medium-bodied lithographic varnishes with, possibly, the addition of some heavier-bodied vehicle composed of either a natural or synthetic resin varnish or a heavy-bodied lithographic varnish. The vehicle is blended to impart proper distribution of the ink on the press and also to give sharp printing qualities when used on all kinds of paper stock. The pigment concentration is higher than that used in news or cylinder press inks.

**Cylinder press inks** are manufactured with thinner-bodied lithographic varnishes than are used for job press inks. The composite vehicle used in these inks is composed of medium- and thin-bodied lithographic varnishes with compounds made of wax or greases added to impart proper distribution of ink and improve printing qualities. These inks are made in this manner so as to eliminate offsetting and picking of the stock, as this type of ink is used in the printing of all kinds of paper and cardboard. When making these inks for two-color printing (one color applied over another color), the first color printed must not dry too fast or hard so as to present a receptive (slightly tacky) surface for the next color. Time of drying is an important factor, as the first printing may lie in the press pile for twenty-four hours before the second color is printed. The second color is manufactured similarly to the first, but with proper tack for overprinting on the first color.

**Process printing inks** are manufactured with thin- and medium-bodied lithographic varnishes, pigments, compounds, and driers. The kind and amount of vehicles and driers used depend upon whether the ink is to be employed as a first, second, third, or fourth down color. The first color of process printing is usually a yellow, either opaque or transparent but slow-drying. The second color is usually a transparent red, manufactured similarly to the yellow, with a slight increase in the amount of driers. The third color is usually a transparent blue made similarly to the first and second color, with a small amount of tacky varnish added, and faster drying than the first two colors. The fourth and last color is a fast-setting black without too much blue tone.

Another method of process printing is to reverse the above method of press routine. The black is printed first, with either the red or

blue following as the second or third colors. The fourth and last color is a transparent yellow. When printing the colors in this reverse order, the inks are made similar to those discussed above, for first color, second color, third color, and fourth color.

The four-color printing press requires inks especially formulated for this progression of printing—printing one color immediately after the other almost simultaneously. The first color—the yellow—is formulated with light- and medium-bodied lithographic varnishes and compounds for fast-setting properties. The next three colors—the red, blue, and black—are made of medium-bodied lithographic varnishes and compounds so adjusted as to enable these inks to trap or over-print one another without smudging, but setting enough until the four colors are printed. The drying of the above inks is controlled by the proper addition of compounds and driers.

Other types of process inks are those used on two-color cylinder presses. This press makes use of two differently constructed inks, printing one immediately after the other, almost a simultaneous action. The first color is printed from the first cylinder, and the sheet is then transferred to a transfer cylinder which carries the sheet to the second cylinder, and the second color is then printed over the first color. The first down color is made with medium-bodied lithographic varnishes, compounds, and a considerable amount of heavy-bodied lithographic varnish to give tack. This enables the second color, which is made similarly to a cylinder press ink, to print sharp and lie smooth on the first color. Drying of these two inks is similar to cylinder press inks, depending on the stock on which they are to be printed.

The inks used on high-speed cylinder presses are usually composed of medium-bodied lithographic varnishes and heavier-bodied lithographic varnishes and compounds. These inks have a medium-bodied consistency between that of a job press ink and a cylinder press ink. The setting and drying of these inks must be very rapid, so as to allow the printing of the reverse side of the sheet in the shortest possible time.

**Bond inks** generally contain heavy- and medium-bodied gum varnishes, medium-bodied lithographic varnishes, high pigment concentration, driers, and compounds to impart setting qualities. They are formulated to dry in 12 to 15 hours (overnight).

Bond inks are generally used in printing letterheads, business cards, and policy and ledger papers. When formulating inks, we must remember that bond papers have a very hard non-absorbent surface and require a fairly heavy-bodied ink.

### Intaglio Inks

**Steel Dye Embossing Inks.** The vehicle is different from that used in printing ink; it is usually made by blending natural and synthetic resin vehicles for hardness and toughness, and solvent to give rapid drying by evaporation. These inks are used to produce the highest grade of business and social stationery. This type of ink is made up of fillers and colors which are usually employed in printing inks.

In these inks a die, either engraved by hand or etched with acid, furnishes the design. The die is inked and the surplus ink wiped away with a wiping pad. The impression is made by pressing the paper between the inked die and a counter. The counter is a male die, made of several thicknesses of cardboard and cut by the operator so as to be able to apply pressure where needed to transfer the ink from the die to the paper.

**Plate Inks.** The formulation of these inks is similar to that of steel die embossing inks, the difference being that the volatile of the vehicle used in steel die embossing inks is replaced by plate oils of various viscosities and driers.

In plate printing the entire plate is inked by a roller, and the surplus ink is wiped away with a cloth. Then the plate is polished by hand, the plate printer using whiting on the palm of his hand to facilitate this polishing. This type of printing is used to produce the highest grade of wedding stationery, bond blanks, and currency.

Another method in plate printing is the intaglio process. This includes rotogravure, both from cylinders and plates. In the formulation of these inks, the pigments used are the same as mentioned in the making of the steel die inks, but the vehicle contains more volatile and is correspondingly faster drying.

### Planographic Inks or Lithographic and Offset Inks

Lithography was invented in 1796 by Alois Senefelder of Bavaria, and is based on the fundamental principle that oils and greases are mutually repellent with water.

Lithographic and offset inks, like other types of inks, are essentially a dispersion of pigments throughout a vehicle. The vehicle is usually composed of lithographic varnishes, driers, and waxy materials, and, in some instances, oleoresinous vehicles. Although linseed oil, as lithographic varnish, is chiefly used, perilla and tung oil are also employed, but to a smaller extent. As already indicated, the heat-bodied (lithographic varnishes) and not the raw oils are used in the inks.

The pigments are ground in the vehicle on water-cooled steel roller mills (see Chapter 23) until thoroughly dispersed. The proportions of the pigments and vehicle may be varied to obtain an ink of proper consistency, which is considerably more viscous than typographic ink. Offset printing makes use of a thin film of ink since only a portion of the original film on the plate is transferred through offset from the rubber blanket to the stock or material being printed. Owing to this fact, these inks should be formulated with maximum color strength and high pigment-to-vehicle ratio.

A surface such as stone or metal is treated so that it has a slight grain. A design or lettering is placed on by a waxy solution, crayon, or transfer process. The non-printing surfaces are treated with gum arabic or albuminous solutions, and the printing surface is rolled with a heavy lithographic ink. This process may be repeated with an acid re-etching process to accentuate sharp lines. The printing process is a rhythm of dampening-inking-printing-dampening-inking-printing, until the run is completed.

The Lithographic Technical Foundation, Inc., in its article "Ink Relationships" (13), claims that since the service the ink renders is necessarily conditioned by the mechanical devices on the press set up for its distribution, it follows that such devices and the ink must work together harmoniously. A lithographic and offset ink must transfer readily from one roller to the next and from the form rollers to the surface of the design plate. The ink must then transfer readily to the design and the lettering on the plate without adhering to the remainder of the plate, which is dampened with water, then transfer sharply to the rubber blanket and from this surface to the paper or other material being printed. But, it is equally important that it should not transfer too readily, to avoid printing a heavy film of ink with the subsequent loss of high lights and printing value of the image.

With reference to the plate, the ink must be of such consistency that it responds readily to the ink-attracting qualities of the developed portions (design and lettering) of the plate, yet not be so greasy or soft as to affect the undeveloped portion.

It is necessary that proper balance be maintained between the affinity of the ink for the plate and the blanket; it is also necessary that the balance be proper between the affinity of the ink for the blanket and the paper. In other words, the ink must possess adequate adhesive and cohesive properties. It must split or separate with sufficient readiness to enable it to transfer from the plate to the blanket and from the blanket to the sheet; but, at the same time, it must be



sufficiently stiff or free from greasiness to print cleanly and distinctly and not expose the blanket unnecessarily to the harmful effects of constant contact with greasy ink. The ink must also dry with the desired finish within a definite time and be able to adhere over other colors, or to trap inks afterward. It is also important to use those pigments that do not bleed in water and vehicles that will not emulsify readily with water or water solutions used on the lithographic damping rolls.

During the printing process a slight emulsion of water in the oil or vehicle of the ink is formed. Whenever it inverts to the oil-in-water type of emulsion, washing or scumming takes place.

The disadvantage of this reaction is that the emulsion carries particles of pigments to the undeveloped portion of the plate, which, in turn, colors the non-printing portions of the stock being printed. This change in the type of emulsion is largely influenced by surface tension of the vehicle and the interfacial tension between vehicle and water, between pigment and water, and between pigment and vehicle.

Ink failure may very easily be due to the paper used in lithography. Thus it is essential that stocks be chosen that work best with the ink or the color proposed for the job. There are various types of paper used, the most common of which will be found listed in the paper section.

The drying of lithographic inks is due to some evaporation and absorption, but mainly by oxidation, with polymerization and condensation. A recognized disadvantage in using excessive amounts of liquid driers in these inks is that they sometimes contain water-soluble salts that may attack the zinc plates. Evidence of their action is noted by discoloration in the plates. This often occurs with the excessive use of cobalt drier, especially in black, with its proclivity to slow drying. A mixture of a surface drier, such as cobalt, and a through drier, such as the lead paste driers, generally overcomes this difficulty.

The manufacturers of printing inks and the printers must give serious consideration to the many factors which govern the making and the application of the inks. These factors, as listed by the Lithographic Technical Foundation, Inc., in its article "Ink Treatment" (13) are:

1. Nature of the various inks.
  - a. Opacity or covering power.
  - b. Specific gravity of relative bulkiness.
  - c. Working quality.
  - d. Tendency to brilliancy or dullness.

- e.* Drying properties.
  - f.* Degree of permanency.
- 2. Type of paper or material printed.
  - a.* Highly coated stock.
  - b.* Slightly coated stock.
  - c.* Offset papers.
  - d.* Bond.
  - e.* Right or wrong side of stock.
  - f.* Metal (coated and uncoated).
- 3. Type of design.
  - a.* Large solids exclusively.
  - b.* Small solids exclusively.
  - c.* Solids and open work combination.
  - d.* Open work exclusively.
- 4. Number of the color on the job, i.e., 1st, 2nd, 3rd, etc.
- 5. Speed of press.
- 6. Length of time between printing of one color and the next.
- 7. Type and condition of blanket.
  - a.* New or used.
  - b.* Firm or resilient.
- 8. Temperature and humidity of press room.
- 9. Type and condition of form rollers.
- 10. Strength of damping solution used.
- 11. Depth and type of grain on plate.

The limitations and exact specifications as to pigments, varnishes, and compounds that are used in lithographic and offset inks are greater than any in other type of ink except special typographic inks that must withstand the soap, alkali, or food tests.

### General Inks

Metallic inks are applied by either letterpress, offset, or intaglio method. It is most important to use the most brilliant lining bronzes in these inks. The correct proportion of the linings to the vehicles is governed by the press and paper stock used. The lining bronze is generally mixed thoroughly with the minimum amount of vehicle and then thinned with additional vehicle to a viscosity similar to that of a cylinder press ink.

**Lacquer Printing Inks.** The use of cellulose base inks is of recent innovation for specialized types of printing where solvent or aniline inks are used.

In these types of inks the cellulose with a plasticizer is mixed with the necessary pigments and ground. The solvent portion is added later, or the entire batch is ground in a pebble or ball mill.

For fast-printing rotary presses with closed fountains this type of ink works very well on glassine, cellophane, or hard-finished stocks. The cellulose base takes the place of natural or synthetic resins and meets more effectively the requirements of faster setting, hard drying, and heat resistance. Various resins may be added to increase gloss and durability when required.

### TESTING PRINTING INKS

In most cases it is found most advantageous to test the ink according to customers' specifications and on the paper stock or material that will ultimately be used.

**To judge body and flow,** take  $\frac{1}{2}$  ounce of ink on a glass plate at room temperature, 75° F., and dip the spatula in, noticing the length of string and time taken by the ink to level off. This will give a relative idea of body of the ink, and spread on rollers and plate, and should be compared with a standard.

**Tack** can be estimated by patting out some ink with the middle finger on the stock to be used. If too tacky the surface will pick and if too soft the finger prints will be blurred.

**Grittiness.** Take an unused can, open it, and remove the top paper and also top layer of ink with a clean spatula. Scrape the spatula across the ink, and rub some of the ink on the blade of the spatula. If there is no grain on both surfaces when examined under a light at a 45-degree angle, the ink is well ground.

**Drying.** Pat out or print out ink on stock to be used. Check hourly and note when the ink is dry to the finger. Also note relative setting of the ink.

**Comparing Color Shade.** A comparison for shade of a printing ink should be made with a standard sample. A drawdown (see Fig. 2) of both inks in juxtaposition is made on 16-pound bond paper. This is done with a 3-inch broad blade knife in such a way as to show 1 inch of masstone and 3 inches of undertone. If the drawdown is made on bond paper on which a black strip is printed, an examination of the ink coverage over the black will give a relative comparison of the opacity or transparency of the two inks.

As a further check on shade and for strength comparison, the ink is mixed with zinc oxide paste ink containing driers. The proportion

depends on the strength and specific gravity of the ink to be tested; generally fifty parts of white ink to one part of colored ink suffices. These mixtures are then drawn down and compared.

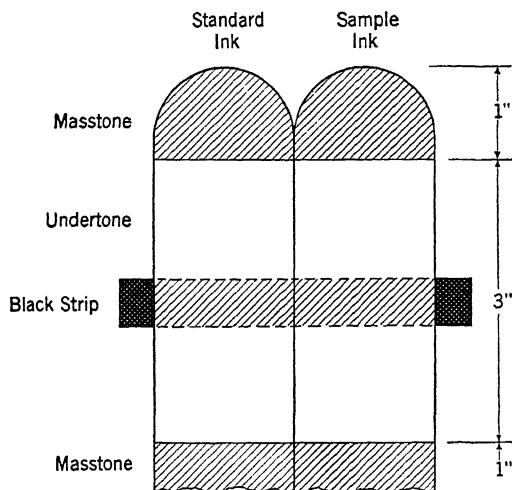


FIG. 2.

When determining the resistance of an ink to light, a dried print is exposed to artificial light (the mercury arc lamp and the modified

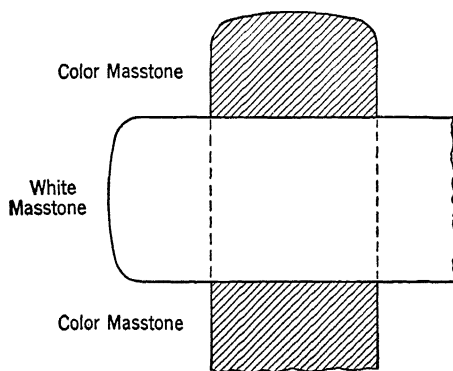


FIG. 3.

carbon arc) and also natural light, such as it would receive in actual usage (to be discussed in detail later).

Varnish bleed can be checked by criss-crossing at an angle of 90 degrees a drawdown (see Fig. 3) of the ink with an opaque white and,

when dry, discoloration of the white is noted and compared with the standard.

The test for water bleed can be applied for lithographic ink. A portion of the wet ink is placed in a test tube or pan with a quantity of water or lithographic fountain solution and agitated for a few hours. The liquid is then drawn off and noted for bleed or scum of the ink.

When testing an ink for alcohol bleed or resistance to lacquer solvents, dried prints of the ink and standard ink are immersed in separate tubes of the test liquid for a specified length of time, 1 to 8 hours, depending on the requirements and solvent action of the test liquid. A comparison of the prints and discoloration of the liquid is made with the standard and noted. Another method is to spot a dried print of drawdown of the ink with alcohol or a lacquer solvent, allowing it to streak across the ink to the clear paper. The bleed can be noted and compared on this portion of the paper.

The test for paraffin bleed is made by dipping a solid print of the ink into a paraffin bath at 120° F. and also 200° F., allowing the paraffin to drain from the colored area to the unprinted area. A comparison of the bleed is made in the solidified paraffin with the standard.

When testing an ink for grease bleed, a thoroughly dried drawdown or print on paper, specified by the customer, is placed face down on the grease, also specified, for 24 hours at the temperature the printed matter will be subjected to in actual use. After removal, any tendency to bleed or discolor the grease is noted. This test also applies to soap wrapper inks by substituting a specified soap for the grease and allowing it to stand in a moist atmosphere for 24 hours.

The resistance of an ink to acid and alkali can be determined by immersing dried prints in 2 per cent sulfuric acid, 6 per cent acetic acid, and 2 per cent chromic acid for 15 minutes and in 1 per cent, 2 per cent, and 3 per cent sodium hydroxide for 20 minutes. The print and solution are compared with the standard and a blank check made in water; any discoloration and bleed are noted.

When testing an ink for its resistance to heat or its ability to bake, the temperature and the length of time of baking should be used as specified by the customer. Panels are prepared by rolling out the ink on plain and white coated tin. The panels are then baked for the specified time and temperature, usually 250° F. for 12 to 15 minutes, and compared with dried unbaked panels. To determine maximum baking temperature, other panels are baked 15 minutes each, at increasing temperature, until complete color change or breakdown is reached.

Perhaps the inks that must withstand the most rigid requirements are those used for parchment printing. Colors play an important part in the manufacture of these inks. The colors must not only be impervious to the materials to be wrapped, because the wrappers come in contact with the foodstuff, but they must also withstand any pretreatment or aftertreatment accorded these wrappers.

Because of the extreme conditions these inks may encounter, and the rigid requirements, it is easy to understand that there are relatively few pigments possessing the necessary properties for their use.

### COLOR RESISTANCE TO FADING BY LIGHT

Accurate knowledge of the color resistance to fading by light of printing inks is essential, particularly for out-of-door posters. The chief factors are:

1. The photochemical reactions of the varnish, and the colors under actinic or heat rays of sunlight. These rays rearrange the molecular structure of the color particles, causing the color to disappear. Also, the same rays break down the varnish and, with the formation of peroxides and nitroso compounds, there is a further destruction of color and film values.

2. Humidity, heat, and destructive gases increase the rate of these processes.

3. Pigment dilution with white, or non-opaque, fillers decreases the resistance of the color pigment, causing rapid fading. As the sunlight and its ultraviolet radiation varies from day to day, and in various locations, it is difficult to arrive at a standard test method. We have the mercury arc lamp and the modified carbon arc as the two best standardized working sources. However, neither is truly representative of sunlight, and the results obtained should be correlated by actual experience.

4. Acid or alkaline paste applied to the printed matter will destroy colors sensitive to their reaction.

Some vehicles, particularly those of high gloss synthetic or neutralized fossil resin formulation, are especially effective in protecting the pigment from the effect of the actinic rays. They also protect the pigment from moisture, as high atmospheric moistures accelerate destructive chemical reactions. In making colors, one quite often matches with a toner, reduced with white non-opaque fillers (extenders) or other suitable pigments. There are points of reduction with most of

these toners where they rapidly fade when exposed to light. The resistance to fading of the toner drops very rapidly out of all proportion to the ratio of reduction. Also, the heavier the film of ink applied the more intense the color, and the greater the resistance to fading. It is well known that some color combinations can be made of those pigments which individually have non-fading property, yet because of chemical action between them lose this non-fading characteristic. This is true of nearly all pigments when used on certain bases. In testing colors in the open sun for thirty days, we have a fair measure of their resistance to light (non-fading) and classify them as follows:

*Class I—Light Resistance—Excellent*

Carbon black, earth colors, English vermilion, orange mineral, cadmium yellow and red, zinc yellow, ultramarine blue, chrome yellow, chrome orange, chrome green, molybdate orange, iron blue, madder lake, hansa yellow, toluidine toner, chlorinated para toner, phthalocyanine blue.

*Class II—Light Resistance—Very good*

Para red toner, lithol rubine, pigment scarlet, phosphotungstic blue, purple, green, and rhodamine.

*Class III—Light Resistance—Good*

Barium red lake C, calcium lithol toner, barium lithol toner, sodium lithol toner, tartrazine yellow, alkali blue.

*Class IV—Light Resistance—Fair*

Sodium red for lake C, yellow lake, naphthol yellow lake, scarlet lake red, acid green lake.

*Class V—Light Resistance—Poor*

Tannic acid lakes, bromo acids lakes, eosine reds, phloxine lakes, methyl violet and peacock blue lakes, methyl violet, persian orange.

## PAPERS AND PRINTING INK

The best grade of paper is necessary for the attainment of highest quality in printing. It is also necessary to select printing ink compatible with both the type of paper being printed and the type of press being used. One of the most important characteristics pertaining to quality printing is the manner in which the ink is absorbed by the paper surface. In this respect the absorption property of a paper should be mentioned only in relation to a definite ink, as inks of varied consistency and vehicle composition will give widely different absorption properties for the same paper. For this same reason, the penetrating power of an ink should be mentioned only in respect to a defi-

nite paper surface as the same ink will have different penetration on various paper surfaces.

Uniform thickness of the ink film is another important feature toward perfect printing. The ink film on the paper is extremely thin, and a variation in the thickness of the film as small as 0.002 mm. will present a noticeable difference in shade.

Another feature that must be taken into consideration is the type of ink necessary for the brown or dark-colored cover stocks, as these will affect the shade of an ink considerably. These inks are formulated with opacity to cover the colored stock and allow the true color of the ink to predominate with minimum change. Opaque inks are also used on uneven surfaces where there are high and low areas, as opacity helps toward a more even impression, whereas a less opaque ink would print dark on the low surfaces and light on the high surfaces, thereby presenting a mottled print.

The following glossary adapted from a paper prepared by James D. Studley, Chief of the Pulp and Paper Section, Forest Products Division of the United States Department of Commerce (23), is presented in order to clarify some of the terms commonly used in the pulp and paper industry. In addition, indication is also given of the inks used on each paper.

**Absorbent paper.** An unsized, loosely felted paper made to absorb water or other liquid. It may be made of either rag or wood fibers, specially cooked to make them soft. Blotting papers, filter papers, toweling, facial tissues, and sanitary napkins are in this class.

The inks used for printing on this type of paper are generally manufactured with a soft body and little tack, so as not to pull the loose fiber of the paper. Bleeding of the ink must be controlled, because of the absorptive qualities of the paper. Driers may be kept at a minimum as the ink dries mainly by penetration.

**Bag paper.** Any paper used for bags. Usually a kraft paper because of the strength factor, but it may be glassine, wood manila, sulfite wrapping, or even tissue paper.

The inks used on paper bags are discussed under the separate papers used.

**Bagasse.** The stalk of the sugar cane after it has been crushed and the sugar removed. Bagasse is a by-product of the cane sugar industry; and it is used by, at least, one large company in the manufacture of insulating board.

This type of board is not used for printing.

**Binder's board** A single-ply, solid board made on a wet machine from mixed papers, and generally used in book covers. Various thicknesses are obtained by pasting together requisite number of sheets.

This board is not printed on directly, as book covers are coated with plain or impregnated cloth.



**Blotting paper.** An unsized, loosely felted, absorbent paper used for blotting purposes. Originally made from a good grade of rag pulp, it is now largely made of chemical wood pulp.

The inks used on blotting paper are covered under absorbent paper; however, most blotting papers have a top covering of coated paper whereon the printing is done. The inks for use on this type of paper are similar to those discussed under *Coated paper*.

**Board.** A general classification designating the product of a paper machine 0.012 inch or more in thickness. It is made principally on a cylinder or a wet machine from wood pulp, straw, and waste papers, and may contain rags or other fibrous materials. Among the common requirements are strength, durability, stiffness, or flexibility, and a surface adapted to printing.

Carton board inks are formulated to flow freely with medium and thin bodied lithographic varnishes, wax compounds, driers, and a percentage of hard drying gum varnish. By manipulating the driers and gum varnish, a hard surface can be obtained on the ink. This resists the abrasive action of the filling and gluing machines used on the printed cartons and also avoids rubbing during shipping. Pigments are chosen with reasonable permanence to light and resistance to the action of the product the carton will contain. If the board is uncoated, it is generally dark; therefore, an opaque ink is resorted to.

**Bond paper.** A writing paper, hard-sized and designed for pen and ink use. It is quite generally used by the business office for letterheads, legal documents, and other uses where writing quality, appearance, and strength are important.

The inks manufactured for bond paper have good color strength, heavy body, and a fair amount of tack. Heavy and medium bodied lithographic varnishes, heavy bodied gum varnishes, and wax compounds are included in the formulation with a good percentage of driers, as these inks dry entirely by oxidation due to this stock being non-absorptive. Another type of ink used on bond paper is die stamping ink. This type of ink is generally used for stamping letterheads. Die stamping ink is manufactured with a thin viscosity and dries rapidly by evaporation with some oxidation. The vehicle is formulated with resins, both natural and synthetic, in solutions with petroleum solvents, waxes, greases, thin bodied lithographic varnishes, and a percentage of driers.

**Book paper.** A printing paper used, as the name signifies, for books, magazines, and similar purposes. May be coated or uncoated.

Inks for this paper are formulated with minimum tack and proper penetration for the grade of stock, speed of press, and the nature of the work being run. There must be enough penetration to prevent offset and yet not enough to make the printing visible on the under side of the sheet, as this side may also receive printing. The vehicle generally contains variable quantities of mineral oil and lithographic varnishes, with or without synthetic resins. Black inks generally contain rosin oil and rosin varnishes.

**Boxboard.** Any board used for paper boxes or cartons. Made of mixed paper stock, chemical pulp, or straw pulp. It is essentially of three classes: 1, container board; 2, set-up boxboard, or 3, folding boxboard.

Boxboard or carton inks are discussed under *Board*; however when formulating the ink, tack, penetration, and drying must be compatible with the type of boxboard being printed.

**Bristol Board.** A general term applied to certain types of cardboard having a thickness of 0.006 inch or more. There are three classes of bristols: (1) Fourdrinier bristol, (2) cylinder bristol, and (3) wedding bristol, a pasted sheet.

Inks used for this stock are similar to those discussed under *Board* and *Boxboard*.

**Building paper.** A heavy paper designed to prevent the infiltration of air and moisture in building construction. It includes sheathing paper, roofing paper, and felt paper.

This type of paper is not used in the printing industry.

**Cardboard.** A class of heavy papers made on either a Fourdrinier or a multi-cylinder machine, or by pasting two or more piles together. Cardboard may be coated or uncoated.

Inks used are discussed under *Board* and *Boxboard*; however, when formulating inks for the coated variety, tack must be kept at a minimum yet not so small an amount as to prevent distribution on the press. Excess tack will pick the coating, thereby producing spotted prints, and the particles of coating will fill up the type and plate, necessitating frequent wash-ups.

**Chipboard.** A board used for many purposes where high finish and strength are unnecessary. It is made from waste papers, usually mixed papers, and may be a solid board or may be lined on one or both sides with a different grade of stock.

Inks for this stock are similar to those used on *Board*, *Boxboard*, and *Cardboard*.

**Cigarette paper.** An unsized tissue paper, usually made from cotton, linen, or hemp fibers, used in the manufacture of cigarettes.

**Coated paper.** Paper which has been coated with clay or other mineral substance and an adhesive, usually casein. Coated paper is used in books, magazines, and catalogs, where a smooth surface suitable for halftones is desired.

Inks for coated paper are formulated with a mixture of medium and thin bodied lithographic varnishes to produce a medium bodied ink, a percentage of wax compound to prevent offset, and sufficient drier, as these inks dry mainly by oxidation. The tack should be adjusted so the ink will print sharp and clean halftones and small type matter. If the body of the ink is too thin, or there is too little tack, fine type will not print sharp and a halftone cut will gradually fill up with ink between the dots and soon print a flat solid. If the body of the ink is too heavy and has excess tack, the ink will tend to remain too much on the surface of the stock and cause offsetting. The excess tack will pick the coating, thereby producing spotted prints, and the particles of coating will fill up the type and halftone screen, necessitating frequent wash-ups. The pigments used are generally of fine particle size and easy grinding characteristics.

**Containerboard.** A built-up board consisting of "jute" or kraft liners for the outer surfaces and chipboard or a corrugated medium for the center. It is used in the manufacture of shipping containers.

Inks for containerboard are in a fairly thin body and dry on the surface of the board with a hard glossy finish. The vehicle is generally formulated with a thin lithographic varnish, mineral oil, rosin oil, rosin varnish, other vegetable oils, waxes, and synthetic resins. A good percentage of drier is added, for hard drying and tack should be controlled as an excess will rupture the board by pulling the surface loose from the corrugated inner part.

**Corrugating material.** A board, generally 0.009 inch in thickness, used for the corrugated or fluted sheet of double-faced corrugated boxes. It is generally made of straw, kraft, chestnut, or similar pulp.

This material is not used for printing; see *Containerboard*.

**Cover paper.** A chemical wood pulp or rag paper used for the cover of pamphlets, books, catalogs, and the like.

**Cover inks.** Are made with medium- and heavy-bodied lithographic varnishes, with maximum opaque pigment, and compounds for penetration, absorption, and easy flow. Suitable driers make the surface dry hard, so as to prevent rubbing in handling the finished product.

**Engine sized.** Any paper in which the sizing is added to the pulp before the paper is made.

**Esparto.** A grass of southern Spain and northern Africa which is used in Great Britain and Europe as a source of pulp for book paper.

**Felt.** A bulky, rough, cheap paper designed for saturating or sound deadening. It is usually made from low grade rags and mixed papers. Not used for printing.

**Folding boxboard.** A term applied to any grade of board that can be made into folding boxes without breaking or cracking.

Inks for this stock are discussed under *Board*, *Boxboard*, and *Cardboard*.

**Glassine.** A supercalendered, glossy, transparent paper made by the long-continued beating of sulfite pulp. This long beating so changes the pulp fibers that they become almost gelatinous. Glassine is highly transparent and is used in transparent bags and as wrapping materials.

Inks for this stock must dry entirely by oxidation, owing to the non-absorbent properties of glassine. They must dry with a hard, tough surface and be resistant to rubbing and scratching. The inks must have good color strength and may be either transparent or opaque. The vehicle is generally formulated with medium-bodied lithographic varnish, tung oil, perilla oil, synthetic resins, a percentage of concentrated driers, and a possible small percentage of solvent to increase the compatibility of the ink for the surface of the stock. Other types of inks used are the rapid-drying aniline inks. They are composed of coal tar dyes dissolved in organic solvents, plasticizers, shellacs, and synthetic resins. Their properties include extreme brilliance, strength of color, flexibility, adhesion, hardness, and speed of drying.

**Greaseproof.** A paper resistant to oil or grease, used largely for wrapping foods and other products of a greasy nature. It is usually made of sulfite pulp, well beaten. Greaseproof paper does not include the waxed papers. Parchment paper is a greaseproof paper.

Parchment inks are formulated with a fairly heavy body and excellent adhesion for printing. The vehicles and pigments used should be as impervious as possible to the action of the material on which the finished prints will be used. The vehicle is generally composed of a medium-bodied lithographic varnish, tung oil, perilla oil, synthetic resin, mineral oil, wax compound, and a percentage of strong drier.

**Groundwood.** A pulp made mechanically by grinding wood against a grindstone.

**Hanging paper.** A ground-wood-sulfite paper made primarily for wallpaper.

Inks for this paper are of a very thin body and dry mainly by penetration. Only those pigments most permanent to light are used. The vehicle is generally

composed of thin lithographic varnish, raw linseed oil, thinners such as turpentine and petroleum spirits, and a percentage of driers.

**Kraft paper.** A paper made of unbleached sulfate pulp, which, because of its strength and toughness, makes an excellent wrapping or bag paper.

Kraft inks are manufactured to a medium body and dry both by penetration and oxidation. Owing to the toughness of the paper, the ink may have a fair amount of tack but not enough to pull the fibers of the stock. These inks are formulated with opacity to reduce discoloration by the brown color of the kraft, thereby producing cleaner and more brilliant colors. The vehicle is generally composed of thin and medium-bodied lithographic varnishes, gum varnishes, wax compounds, and a percentage of driers.

**Kraft pulp.** An unbleached wood pulp, usually brown in color and of superior strength. It is made by the sulfate process.

**Lignin.** One of the two chief components of wood, the other being cellulose. The cellulose fibers make up the portion used for paper making.

**Loft dried.** A paper dried without tension by hanging in a drying shed or loft, subsequent to tub sizing.

**Manila.** A term used to designate a characteristic light brown color formerly associated with manila fibers.

Inks used are similar to those used on *Board*, *Boxboard*, and *Cardboard*.

**Matrix paper.** A heavy, unsized, unfinished paper used to make the mats into which the melted type metal is poured when printing-press plates are cast by the stereotyping process.

**Mechanical pulp.** Synonymous with ground wood.

**Newsprint paper.** A low-grade printing paper, made principally of ground-wood pulp and containing approximately 20 per cent of unbleached sulfite pulp.

News inks are extremely thin bodied and dry principally by penetration into the highly absorbent newsprint paper. They are formulated with carbon black, a possible addition of blue toner and mineral oils, with or without the addition of some rosin varnish, as the vehicle.

**Overissue news.** Printed newspapers from the publishing plants which have never gone into circulation, hence are clean. Should not be confused with old newspapers.

**Pasteboard.** A term applied to both boards and cardboards that are formed by pasting a liner on cheap stock. The term is popularly used to denote any stiff board of medium thickness.

Inks for the printing on this stock are similar to those used on *Board*, *Boxboard*, and *Cardboard*.

**Pressboard.** A stiff, smooth, hard-surfaced solid board which approaches vulcanized fiber in texture.

Inks for this stock are formulated to a medium body, and because of the hard printing surface, a fair amount of tack. The ink must dry entirely by oxidation, owing to the non-absorbent properties of the board. The vehicle is generally composed of medium lithographic varnish with a large percentage of rosin or synthetic resin varnishes. Some wax compound is included with a percentage of driers.

**Rosin.** The sticky substance found in the resin ducts of the pines and certain other softwoods. Sometimes found, too, in pockets in these same woods.

**Size.** A material, such as rosin or glue, added to the mixture of pulp and water in the beater, or to the finished paper, to give water resistance.

**Soda pulp.** A chemically made wood pulp in which the cellulose fibers are separated from the wood structure by cooking in a solution of caustic soda.

**Strawboard.** A cheap, coarse board made of incompletely cooked grain straw, commonly used as a corrugating medium for corrugated shipping containers.

This material is not used for printing; see *Containerboard*.

**Sulfate pulp.** Chemical wood pulp obtained by digesting wood with a mixture of sulfate of soda, caustic soda, and sulfide of soda.

**Sulfite pulp.** Chemical wood pulp resulting from cooking wood chips under pressure in a solution of bisulfite of lime.

**Tub sized.** A term applied to paper which has been passed through a bath of glue or starch and subsequently air or loft dried. The glue or starch improves the quality of the paper.

Inks for printing on this type of paper are similar to those discussed under *Book paper*, *Coated paper*, and *Bond paper*.

#### Other Materials Used for Printing

**Cellophane.** This is a cellulose regenerated from the acetate. It is manufactured in various thicknesses, both moistureproof and non-moistureproof.

The inks used are similar to those discussed under *Glassine*.

**Cloths.** These are cloths of various grades and weaves and may be plain, impregnated, or coated. Some cloths are pyroxylin (nitrocellulose) impregnated and coated; others are coated with starch.

The inks used on cloths vary from the heavy-bodied bookbinder's inks which are printed on the cloths mounted on cardboard to the medium-bodied inks that are printed on the unmounted cloths. Some inks dry by chemical combination, others by oxidation. They are formulated with natural and synthetic resin varnishes, medium- and heavy-bodied lithographic varnishes, plasticizers, solvents, and a percentage of driers. These inks are generally manufactured with opacity as most of the cloths printed are colored.

For a fuller list of technical terms relating to printing and paper, see the following books:

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## CHAPTER 22A

### LUMINESCENT PAINT

GILBERT T. SCHMIDLING

#### TERMINOLOGY

Much of the terminology used in the luminous paint industry is ambiguous or inaccurate. The title of this chapter is an example of this, since the flame of a match or other burning or oxidizing bodies at elevated temperatures can correctly be called luminescent. The word *photoluminescence* more correctly describes a class of materials which emit light at ordinary temperatures, after first having absorbed light or other energy at a shorter wavelength. The word *phosphorescence* often implies that phosphorus is present, at least to the layman, and the term *fluorescence* was derived from fluorite. To call any of these materials phosphors is especially misleading. Of all these, the word fluorescence most accurately describes the phenomena meant.

Sir George Stokes, in 1852, thoughtfully and deliberately chose fluorescence to describe certain observations then referred to as "inner dispersion," most strongly exhibited in the mineral fluorite. The literature is extensive, but it, too, abounds in inaccuracies, loose statements, and word descriptions of such factors as intensity, color, duration of afterglow, and controversies as long and exciting as in any other art. This is probably due, at least in part, to the beauty of these phenomena, which have served to attract thousands of investigators in the last one hundred years, not all of whom were given to making measurements. The subject is, however, a complex one, and the main difficulties arise when generalities are attempted, through research on one substance, or even a class of substances. Very few laws have been found which have not been contradicted, or from which one could predict results. Fluorescence can be defined as a phenomenon which occurs in that class of substances, pure or impure, organic or inorganic, which emit light only when the exciting source of light is directed upon them, without noticeable increase in temperature, without permanent chemical change, and in which the action causing frequency



transformation is confined entirely within the atom or molecule. The life of the excited state is only about  $10^{-7}$  or  $10^{-8}$  second.

Phosphorescence refers to those materials which continue to glow after the exciting light is cut off, for a period of  $10^{-2}$  second to several weeks in the case of non-radioactive materials. But Becquerel (2), as early as 1872, reached the conclusion that fluorescence and phos-

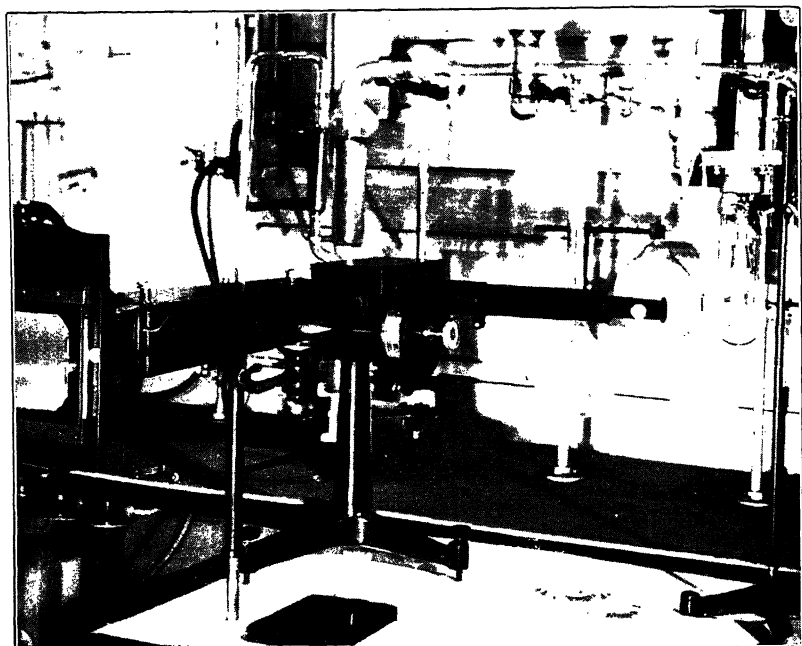


FIG. 1. Spectrum bands and lines become narrower at liquid air temperatures in high vacuum. Shows apparatus used to measure spectral distribution of fluorescence excited by electron beam of 3,000 volts velocity.

phorescence are identical in mechanism. This has since been confirmed by many investigators, but most importantly by Nichols and Howes (23) in their series of important experiments on the uranyl salts.

Another example showing the need for an improved terminology also indicates the present state of our theoretical knowledge of the subject. It was implied above that luminescence covers all glowing bodies, whether or not their temperature was raised to the point of incandescence. Grave doubts could be cast on the present assumption that true oxidation does not occur in self-luminous materials. In addition

to the electrical theory of fluorescence, which is discussed later, E. L. Nichols (22) in 1930 found that oxygen was set free when the exciting radiation was directed upon the material, the radiation therefore acting as a reducing agent. The glow starts when the oxygen cloud recombines with the material. This was confirmed by the author a year later (32) by heating a fluorescent screen in a vacuum, as shown in Fig. 1, and burning it by an intense beam of electrons, which after the passage of time so reduced the salt that fluorescence was hardly discernible. Mercury aspirators were meanwhile drawing off the oxygen as fast as it was released. The tube was then sealed off hot. After it had cooled to room temperature, it was opened suddenly and without electrical connections of any sort, and in the dark a brilliant flash was observed, due only it is believed to the entering oxygen. In this paper we shall concern ourselves with only one class of luminous material and a review, however elementary, of the fluorescent principles which are known to govern this class.

## HISTORY

The very earliest records of self-luminous substances, such as minerals and gems, are still shrouded in mystery. It is difficult to tell, at this distance from that dim past, long before the days of the alchemists, where authenticity begins and black magic leaves off. Diamonds, especially the yellowish ones, exhibit considerable afterglow after exposure to the sun, and it is reasonable to suppose, as Kunz (16) points out, that the ancients observed this phenomenon. Pliny, the Elder, mentions a luminous mineral. The true historical record begins with a cobbler and spare-time alchemist, Vincenzo Cascariolo, who was torn between making shoes and gold. He stumbled one day upon a stone which seemed heavier than usual. Upon heating it, he discovered that it would glow in the dark, "sometimes for as long as an hour," and he was soon able to make it glow at will. This happened in Bologna, Italy, about 1599. The material he had found was impure barium sulfate, partially converted to barium sulfide by heating. Years later, a chemist named Marggraf found an "easy and certain way of preparing it with flour as the reducing agent and heating it in a closed crucible." The story of early discovery is most interestingly told, and in great detail, in a little book entitled *Phosphorescence, or the Emission of Light by Minerals, Plants and Animals*, by T. L. Phipson, published in 1862 and long out of print. The small furor

precipitated by the miracle of the "Bologna Stone," the subsequent intrigues involving princes and even a king, and the confusion of the "philosopher's stone" with Brandt's glowing phosphorus obtained by concentrating urine make, on the whole, one of the most interesting stories in science.

It is little realized today what great philosophic, even medical, importance was once attached to "the stone." It could be called the direct result of the alchemists' attempt to make gold. Luminous materials were reported with accelerating frequency from that time on, until the discovery of "internal dispersion" by Sir David Brewster in 1833 (3). He observed a reddish glow from chlorophyll when sunlight was passed through it. This was followed by Herschel's discovery, in 1845, of the blue glow emitted by quinine sulfate. The connection with luminous solids was not yet apparent. The true significance of these observations were crystallized by a series of brilliant researches by Stokes (38) in 1852, who enunciated the principle that fluorescent light is always of longer wavelength than the exciting light. This is one of the few basic principles upon which all fluorescent theories are founded, but this too has suffered some revision, which will be discussed further on. Stokes later connected these experiments with the phosphorescence of minerals.

The next most important investigator of this period was Becquerel who constructed the phosphoroscope (1), an apparatus for measuring the rate of decay of the phosphorescent light. He soon found that substances thought to be fluorescent only, such as uranium nitrate, actually glowed for 0.03 or 0.04 second after excitation. He also found phosphorescence in such materials as cloth, paper, and dyes. A picture of Becquerel's apparatus can be seen in Atkinson's translation of the classical Ganot's *Physics* (8).

The first exhaustive research on synthetic phosphorescent solids was made by Lenard and Klatt (15). Their work on the alkaline earth sulfides served as the foundation upon which modern luminous paints were developed. The whole subject was reinvestigated by Nichols (5) and his co-workers over a period of years, during which hundreds of important measurements were made. Even a cursory glance at the literature gives one the impression that the early investigators must have been disappointed in their most brilliantly luminous substances. Hopes must often have been high that here at last was the ideal source of light—cold, perfectly diffuse, beautiful. But progress is slow, and only recently have the results of their labors been put to use for the

benefit of mankind. Now it appears that with recent improvements in manufacturing technique of the long afterglow materials, together with the development of more stable vehicles, such as modern plastics offer, renewed interest and activity are in the offing and this class of materials will shortly be important in our economic and social life.

## FIRST PRINCIPLES

### Types of Luminescence

Excluding those radiations due to elevated temperature, luminescence is surprisingly universal. Almost everything around us except pure metal surfaces (even these are possible only in a high vacuum) are luminescent by one form of excitation or another. A few of the less obvious examples are water, ice, snow, freshly cut alkali metals, paper, wood, animal organs, in fact almost all organic materials or their vapors. A complete list would, of course, be practically endless. The various types of luminescence have been catalogued by a number of workers, but, since many substances react to two or more sources of excitation, there is need for a more complete and simplified classification. Many types would be uninteresting to the paint expert and many are only of theoretical importance. In this short paper, we shall confine ourselves to the outstanding examples of each class, and dwell specifically on the type of materials most used at the present time in the manufacture of luminous paints. This will serve, it is hoped, to orient the reader in respect to the position occupied by phosphorescent sulfides to the entire field of luminescence. A further purpose in calling the attention of the paint man to the various types of luminescence is that their usefulness has not even been slightly tapped. Even the sulfides have, until recent times, been used only for novelty purposes. A person of imagination must be impressed by the possibilities of luminous bacteria, for example, studied exhaustively by Harvey (10) and others, and suggested as a source of light by H. G. Wells in his *Journey to the Moon*.

A good example of the possible usefulness of other types of luminescence is shown by the fact that, although the sulfides and uranyl have been more thoroughly investigated than any other type, neither of these is used in fluorescent lighting. In order to eliminate a source of confusion usually found in these classifications, it should be decided whether or not chemiluminescence includes materials which glow because mechanical excitation causes indirect chemical action, for ex-

ample, triboluminescence, as well as materials in which the glow is caused directly by chemical action, as for example in the oxidation of uric acid.

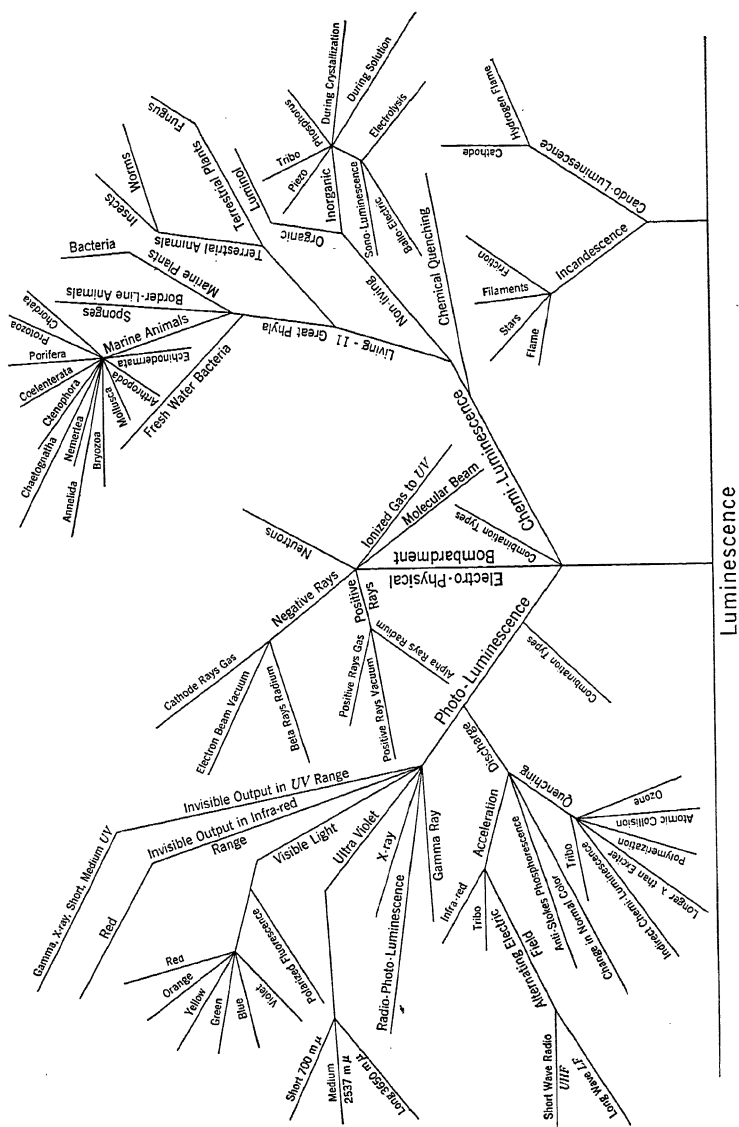
Triboluminescence, caused by friction of fluorescent and phosphorescent crystals, has heretofore been classified as mechanical luminescence. But it must as surely belong to chemiluminescence as the mixture of an acid and a base belongs to chemistry, for, while the causation is mechanical in both, the results are chemical in nature, and in the final analysis, electrical. When triboluminescence is caused by rubbing or grinding activated salts of the alkaline earth metals, the chemical change can be seen with the naked eye. The daylight color of the compound changes, and the fluorescence and phosphorescence are weaker. Reduction occurs, the oxide activator seemingly is ground out of the crystal, with the emission of light. There is another type of triboluminescence in which the chemical change is not permanent. In this type the material is first excited by radiation, then released by mechanical action.

Stating the problem another way, should materials be classified by the type of luminescence which occurs, or by the kind of excitation to which they react? Many materials react to more than one form of excitation. It was suggested by Bancroft in 1913 that chemiluminescence is universal, but it was proved by Nichols (22) that reversible oxidation occurs in all forms of luminescence, even by cathode ray bombardment. Thus, even photoluminescence and electrophysical luminescence are coupled with indirect chemiluminescence, differing only in the type of excitation or the kind of energy interchanged. The separation of such forms as lyoluminescence and piezoluminescence as separate classes is of course untenable. Since all luminescence is chemiluminescence, what then is the difference between the various forms? The key to division is found in the permanence of the chemical reaction and the kind of energy interchanged. Further division can be made by the type of excitation. Luminescent phenomena are divided into two large classes.

#### CLASS A

##### CHEMILUMINESCENCE: PERMANENT CHEMICAL CHANGE

- A-1. Due to interchange of chemical energy, a part of which appears as radiation.  
Requires no external excitation.
- A-2. Due to mechanical excitation.
- A-3. Due to electrophysical excitation.
- A-4. Due to electromagnetic excitation.



## CLASS B

## PHYSICAL LUMINESCENCE: TEMPORARY CHEMICAL CHANGE

- B-1. Due to physical excitation.
- B-2. Due to electric current excitation.
- B-3. Due to electrophysical excitation.
- B-4. Due to electromagnetic excitation.

Class A involves mainly oxidation and reduction in simple cases, but includes the numerous examples of chemical reaction in complex organic and inorganic compounds. This very large field includes all animal luminescence, as exhibited by fireflies and other insects, hundreds of marine animals and plants, luminous bacteria, emission of light during chemical solution, precipitation, and crystallization.

Class B includes photoluminescence caused by electromagnetic radiations. Almost the entire electromagnetic spectrum is included, since luminous effects have been found in all bands except the extreme ends of the spectrum. No luminescence has been reported due to cosmic rays or rays of shorter wavelength than gamma rays, in the range of 0.01–1.4 Ångström (abbreviated Å) units. At the other extreme end of the spectrum, phosphorescent acceleration has been observed in the presence of radio waves a few centimeters long, but no effects have been observed in the broadcasting range. The bands between these two extremes include X-rays, ultraviolet, visible, and infrared rays. Included in this classification are such important forms as thermoluminescence, which causes acceleration of phosphorescence when the temperature is raised, and electrophysical luminescence, caused by physical bombardment. No term has yet been suggested for this class, but the above will convey the meaning sufficiently well for the present purpose.

This type of luminescence is excited by moving particles of high velocity, such as positive rays and negative rays, molecular beams, and beams of ions in which electromagnetic radiations are not involved. Other outstanding forms of excitation in Class B are: positive rays from hot filaments in a vacuum, or an ionized gas; positive rays from radium or other radioactive substances, known as alpha rays; negative rays, including a beam of electrons in a vacuum and a beam of electrons in a gas surrounded by a sheath of positive ions, the combination being known as the cathode ray; beta rays, the negative rays from radium and radioactive materials; and quenching of phosphorescence by red radiation, by alternating electric fields as slow as three

cycles per second, by a high potential electric field, and finally by a high intensity magnetic field.

### SEEING

Because of the relatively low light intensities encountered in luminescent effects, the characteristics of the human eye should be taken into consideration in a study of luminescence. Not that any expertness should be required of the user under normal conditions, but rather because an elementary knowledge of seeing is of assistance in visual evaluation, and especially in the design of phosphorescent materials.

Recent advances in the study of the human eye indicate that seeing is becoming a science in itself, with great ramifications and an already extensive bibliography. Only the more important characteristics of the eye which have a direct bearing on luminescence will be discussed. First and foremost are the causes for variation and brightness as reported by various observers in reference to a given sample of luminous paint. Observer A might say that the sample would glow for five minutes and B would say the afterglow lasted one hour; the maker might say five hours. And they would all be right, provided they were reporting only what they saw and not the conditions under which the observation was made. About twenty to thirty minutes are required for the average eye to become dark-adapted from bright sunshine to complete dark adaptation. At night the length of time is correspondingly less, i.e., corresponding to the intensity of artificial illumination to which the eye has been subjected.

The eye is a wonderful organ, and the reason it can be used comfortably with an intensity range of a million to one is not only due to the action of the iris, which serves only as protection at high intensities of illumination. At low intensities, with the iris wide open, the eye becomes more sensitive with time, during which the visual purple is manufactured. The shape of the crystalline lens changes to a form which absorbs more light. The retina contains a system of double nerves, about five million. One set of nerves, called the cones, is used in bright light and is sensitive to color. In dim light another set of nerves, called rods, comes into play. The rods contain the visual purple, which is very sensitive to light and easily destroyed by it. The rods are not sensitive to color, all colors tending to appear blue-gray. But it appears that photopic, or cone, vision is never cut off completely, and therefore scotopic or rod vision never occurs abso-



lutely alone. The cones are relatively insensitive to light of less than 0.02 foot-candle.

When the dark-adapted eye is again exposed to light the visual purple is destroyed, and above 1 foot-candle cone vision again predominates. Because of these facts it is difficult to demonstrate luminous pigments in the daytime, even if carried out in the dark room, unless the eyes of all observers have been equally adapted. This brings us to a second important characteristic of the eye in connection with luminescence. It was mentioned above that for scotopic vision the eye is not sensitive to color. More accurately, the reason that all colors appear bluish gray is that, under these conditions, the peak sensitivity of the eye has shifted to a shorter wavelength, owing to the filtering effect of the visual purple. This is known as the Purkinje effect. If a number of 60-watt electric lamps are placed in a row, each one radiating a different color of the spectrum, and so filtered that each radiates the same amount of light on an energy basis, then the eye will see the yellow-green as the brightest part of the spectrum. The specific wavelength assigned to this color for the I.C.I. Standard Observer is 556  $m\mu$ . But let these lights be very dim, of the order of brightness of a luminous paint, and the maximum sensitivity of the eye will be in the blue-green and, according to Hecht and Williams (11), the peak sensitivity occurs at 507  $m\mu$ . These are the most accurate data available at the present time on scotopic vision, Moon (21). The very practical result of this effect is that, for equal fluorescent efficiency on an energy basis, a blue-green luminous paint will appear to the eye to be brighter than any other color of paint would be. This is true even if the intensity is so low that it appears blue to the eye, since, because the true color is blue-green, it will appear to be a brighter blue than any other true color could be. Blue-green is definitely the color of the future for low-intensity self-luminous sources, which will probably find their greatest field of usefulness in safety work and other equally important problems in human welfare.

Because of what someone has called "the general cussedness of inanimate things" the very factors which make it possible to increase the apparent intensity (real brightness) of luminous paints operate to make them difficult to measure. Visual photometers cannot be relied upon at very low intensities, and physical photometers do not have the characteristics of the human eye. That is, the latter do not change their color sensitivity with changes in intensity as the eye does. The best compromise at present is to read the first part of the decay curve with a visual photometer, then, when the very dim values are reached,

in the region of scotopic vision, the physical photometer will read these more accurately. It is necessary of course to multiply the galvanometer values by the relative visibility values on the scotopic curve at a given wavelength.

A third characteristic of the human eye, important in respect to studies in luminescence, makes it impossible to compare accurately

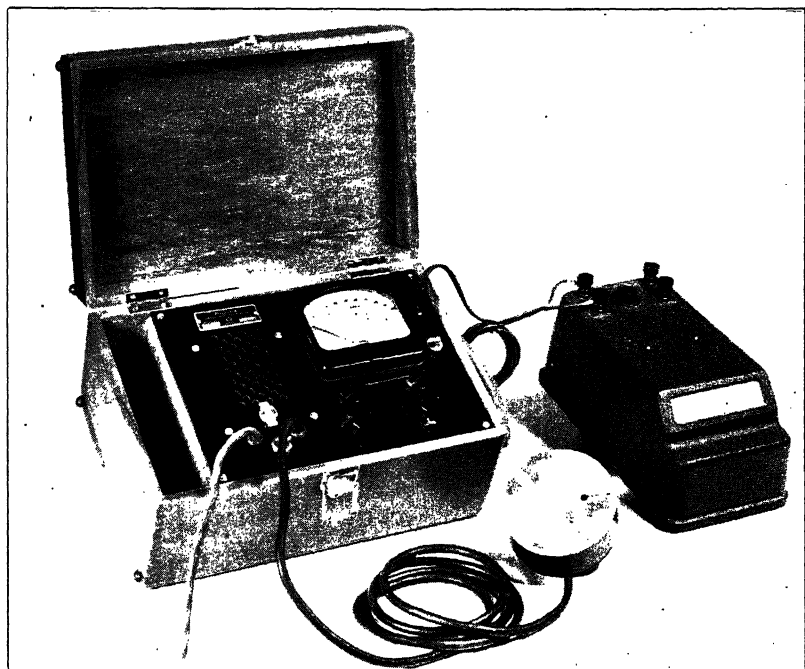


FIG. 3. Photoelectric Photometer.

two samples of luminous powder side by side. When an astronomer wishes to locate a star by the naked eye he does so by looking to one side of it, not at it. This is called peripheral vision. Similarly, if two samples of powder or paint, even though they are of the same batch, are placed side by side, the one looked at directly will be less bright than the other.

Another characteristic of the eye is that the rods of the para-foveal region are not very useful for delineation of form, and square objects of low surface brightness appear rounded off or oval. For this reason, greater efficiency can be obtained for a given area from an oval-shaped object, the largest dimension of which is horizontal. It is recognized

in connection with the design of outdoor plaques that there are two occasions when blue-green is not the most suitable color. During twilight and on moonlight nights the contrast ratio to the blue sky is rather low. Luminous materials, however, are not very useful during these periods anyway, so that this objection, recently raised in connection with the green light on the wing of an airplane, is not valid from the practical viewpoint in the instance of luminous paint, but is important when considering the color of the safety lights on wings.

### THE MOST IMPORTANT EXAMPLES OF EACH TYPE

#### Class A. Chemiluminescence. Permanent Chemical Change

**Class A-1** includes both living and non-living types. These cannot easily be separated at the present time since the luminous substances from some animals continue to glow in the presence of moisture a long time, even years, after the animal has expired.

*Class A-1-A, Inorganic Luminescence, Non-living.* The best example of this class is the oxidation of phosphorus, one of the first luminous materials to be studied. It was separated from urine by Brandt (25) in 1669.

*Class A-1-B, Organic Luminescence, Non-living.* A large number of organic compounds will glow rather brightly when oxidized. Pyrogallol is very effective. One of the brightest materials is luminol, oxidized by hydrogen peroxide; the efficiency is very low.

*Class A-1-C, Bioluminescence,* the production of light by animals, is also a case of oxidation. It is not a vital process, since, as already mentioned, the glow in many cases remains after the animal is dead. Perhaps the one form known to every one is the firefly, about twenty-five species of which exist in the United States alone, and which are characterized in the eastern part of the United States by the family Lampyridae. Thousands of animals are now known which have this property. Harvey (10) states that of seventeen great phyla of the animal kingdom eleven contain luminous forms, so widespread is this faculty. The author has inoculated marine fish with luminous bacteria with a view to obtaining symbiosis in the course of a few generations, but he has not succeeded. Parasitic bacteria, when not symbiotic, lead to the death of the host. One of the most cited examples of luminous symbiosis is an East Indian fish, Photoblepharon, whose bacteria (first studied by Harvey in 1921) live in a special pocket provided for them by the fish. The pockets are located just under each

eye and the animal is able to conceal the lights by drawing a curtain, or fold, over it at will.

The number and kind of luminous objects in the sea are fantastic, ranging from *Noctiluca miliaris*, several of which could be placed on the head of a pin but are nevertheless one of the main factors in luminescence of the ocean's surface at night, through a list of lower and lower animal types, right down to the kingdom of plants. The overwhelming majority of these animals have truly luminous organs of their own. A smaller number harbor luminous bacteria. Beebe saw some of these types in their natural habitat from the Bathysphere. The aquatic forms of luminous animals are almost entirely confined to marine water. Only several fresh-water forms are known; they are bacteria and a worm. A fresh-water Japanese shrimp is luminous by virtue of parasitic bacteria but the union is not symbiotic.

The efficiency of animal luminescence is very low, in spite of occasional statements to the contrary, statements due to a misunderstanding of the terms. All the light of luminous animals occurs in the visible region. Ives (14) gives the firefly a luminous efficiency of 95 per cent. But this means efficiency of illumination, or luminous efficacy. The intensity of light emitted on an energy basis is multiplied by the visibility function at each wavelength. The total efficiency, arrived at by measuring output and input in energy, is very low. This can be measured in animals whose light is continuous, as in bacteria. The efficiency was found to be 0.16 per cent (10), or almost 1 per cent if only that amount of oxygen used in the production of luminescence is calculated. The organs of marine animals are fluorescent by ultraviolet light, 3,650 Å, as are fireflies, but fresh-water fish are only slightly so. The fresh-water species most fluorescent are those low in pigmentation. The author has found (unpublished work) the brightest fluorescence in xanthic form of *Lebistes reticulatus*, and a Gourami of Siam, *Helostoma temminckii*. The surface brightness of animal luminescence (in the highest types of animals in which luminescence occurs) varies between one hundred and one thousand times that of luminous paints—the latter are comparable to plant luminescence, i.e., bacteria and fungi. Ives and Jordan measured the light of a glowworm and found a surface brightness of 14.4 millilamberts. (Luminous paints are measured in microlamberts.) The glowworm is the larva of the firefly, in this case *Photuris pennsylvanica*. The prothoracic organ of *Pyrophorus* (a beetle), according to Harvey and Stevens, has a brightness of 45 millilamberts, but the

brightness of a *Ctenophore mnemiopsis* (species of comb jelly), as measured by Nichols, is only 0.3 millilambert.

These figures cover approximately the brightness range of animal luminescence. Although these intensities seem high when compared to the man-made afterglow materials, the comparison is not a proper one because in the latter the source of excitation is removed during observation. A more proper comparison could be made with the fluorescence of synthetic fluorescent materials continuously excited by 3,650 Å, ultraviolet light, which incidentally is of about the same order of brightness. In this case the luminous animal is far more efficient, but has been surpassed in the case of luminous bacteria by fluorescent sources, such as silicate and tungstates excited by the 2,537 Å line in mercury vapor. A white fluorescent lamp has a coal to light efficiency of three times that of luminous bacteria, and the author (29) publically demonstrated a green source of this type in 1934, utilizing zinc orthosilicate and a hot cathode in mercury vapor, which gave a conversion efficiency of seven times that of luminous bacteria. The surface brightness of bacteria is much lower than in higher forms of life, about 100 microlamberts for a thick suspension in salt water, but it is the only type in which the total efficiency has so far been measured. There is no reason to believe that the conversion efficiency of firefly light is any greater, but, since firefly light, of the yellow-green variety at least, has a greater percentage of its light near the wavelength of maximum visibility, a higher overall efficiency should result. This is one of the most important problems awaiting solution. It is difficult to measure how much energy a firefly actually uses to light his lantern because there are so many other chemical processes going on. According to the naturalist Faber, a part of its food is used for growth, a part is used for manufacturing an anesthetic with which it mercifully kills its prey, usually snails (and incidentally their hard shell it appears able to penetrate), and another part is used to manufacture a chemical which, injected into its prey, dissolves it into a kind of gruel—all these in addition to the manufacture of the best quality of luminous materials. A careful comparison of animal luminescence and man-made synthetic materials shows their progress to be about even in efficiency, with the materials of man in the ascendancy.

Animal luminescence is widely distributed among the various orders, and as is so often the case, no particular family has adopted this property for its own. Some luminous animals are blind, and it is difficult to see of what use their light is to them. Luminous deep-sea fish, at least in the North Atlantic, occur only in the comparatively

thin strata, between 1,000 and 1,600 feet from the surface. It is quite possible that animal luminescence is one of the abandoned evolutionary experiments of nature. Or, as B. W. Smith suggests in his book *The World under the Sea*, fishes may have not long (in terms of mil-

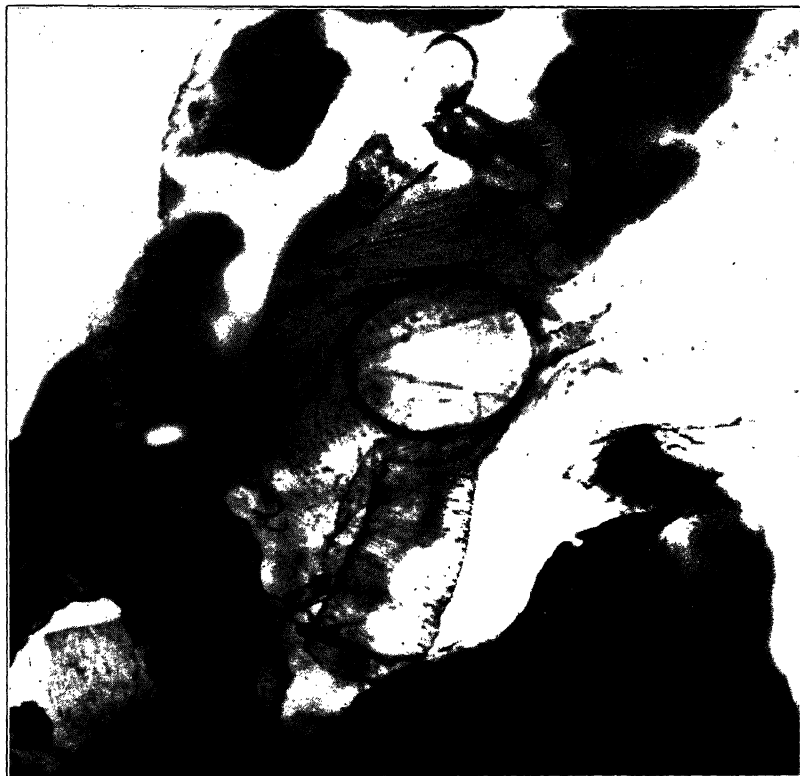


FIG. 4. Branches of Tracheal Tube of Firefly, Lampyridae, at 452 Diameters.

lions of years) inhabited great depths. This would tend to support the theory that the oceanic abysses are by no means an ancient feature of the globe. But William Beebe disagrees with this view. He states (personal communication) that we just do not know what is at the bottom, and that the final answer will very likely not be had until some one can go down there and see. Recent work by Johnson, Brown, and Marshall indicates that certain depths are required to form the proper enzymes for the production of luminous materials.

*Class A-1-D, Crystalloluminescence.* This is difficult to classify, but is placed here because it fits the classification of "permanent chemical change, with emission of light, without external excitation" perhaps more aptly than it fits any other class. It is indirect chemiluminescence. The presence of oxygen is not required. An example is potassium sulfate, which gives off light as it crystallizes. Trautz (40) believes that it is a special case of triboluminescence (see type A-2-A) in which the growth of the individual crystals causes them to rub together, because the light is brighter if the mass is stirred while the crystals are forming. The various effects overlap, however, and the above case seems to have caused a more or less useless controversy because, if it is a case of true triboluminescence, then it is not a case of crystalloluminescence. If they occur together, which is easily possible, then it is not a good example of crystalloluminescence. Any phenomenon can best be studied by isolating it. Triboluminescence can be demonstrated by stirring together activated (not irradiated) zinc sulfide crystals under water. The author is more inclined to agree with Weiser (43), who studied aqueous alkali halide solutions which glow upon addition of hydrochloric acid or alcohol. Weiser believes that true crystalloluminescence is due to the rapid reformation of molecules from ions broken up by electrolytic dissociation, as opposed to triboluminescence, caused by rapid reformation of molecules from ions broken up by violent mechanical disruption of the crystal. For these reasons the subject is placed in this class.

**Class A-2.** A good example of permanent chemical change, excited by mechanical action, with the emission of light, will be called triboluminescence, type A. This type requires no previous excitation and occurs in two main types of materials.

*Class A-2-A.* Pure materials such as uranium nitrate.

*Class A-2-B.* Impure materials such as zinc sulfide activated with manganese. Both these types eventually lose their power to glow by friction when chemical breakdown occurs. The effect can occur in both organic and inorganic materials.

**Class A-3.** Permanent chemical change from electrophysical bombardment.

*Class A-3-A, Pure Materials.* White materials like potassium bromide are quickly changed to a permanent dark color by cathode rays, with emission of light, whiteness again being restored by heating in air.

*Class A-3-B, Lyoluminescence, Emission of Light during Solution.* This was discovered by Wiedemann and Schmidt (42). If crystals of

lithium or sodium sulfate are exposed to cathode rays until they are discolored and then dissolved, a glow will be seen. It is placed in this class because the chemical change is permanent, is coincident with the emission of light, and the glow does not occur at the expense of chemical energy; also because pre-excitation by electrophysical bombardment is required. It must therefore be regarded as a special case of triboluminescence.

*Class A-3-C, Impure Materials.* Chemical reduction by physical particles of high energy also reduces activated salts, with emission of light until reduction is complete. One type, previously undiscovered and noted by the author in 1930, and of which no other record has been found, gives off a much greater light after reduction has taken place. Aluminum oxide activated with chromium was excited by a low intensity beam of cathode rays in the presence of argon gas. After reduction has taken place a very bright light builds up, very much out of proportion to what would be expected from cathode ray incandescence. This did not occur when no activator was present. This was probably a case of candoluminescence under reduced pressure, but further work should be done. Destruction of the fluorescence of radioactive zinc sulfide by alpha and beta rays is another example of this class.

**Class A-4.** Permanent chemical change by electromagnetic radiation.

*Class A-4-A.* The color change observed in some of the unstable mercury compounds was formerly used in X-ray work for timing the dosage. Glass, when a small amount of impurity is present, as manganese, for example, turns a beautiful violet color after a few hours' exposure to X-rays, or a few weeks' exposure to ultraviolet rays from sunlight. Discolored X-ray tubes may be seen in any doctor's office, and beautifully colored pieces of glass may often be found on the beach. Kunzite, a lithium silicate, is unique. Under the influence of X-rays, or ultraviolet rays, it goes through a series of color changes, from the original bluish pink or lilac, to red, blue-red, white, green—then blue-green, and goes through these in reverse order upon heating. The afterglow was measured for 76 hours by Stuhlman and Daniel (39), although these effects were first reported by Kunz (17). This class is unique in that it appears that an impurity activator is necessary for the radiation to cause an emission of light when accompanied by permanent chemical change. There are materials which fluoresce, in the pure state without the presence of an activator, when excited



by X-rays and ultraviolet rays, such as calcium tungstate; but in these cases the chemical change is not permanent. See class B.

### **Class B. Physical Luminescence. Temporary Chemical Change**

**Class B-1, Triboluminescence of the Second Kind, Type B.** This is purely an acceleration process in which the afterglow of an activated salt, after excitation by any form of radiation or cathode rays, will give up its energy at a faster rate upon mechanical agitation. This is the mechanical analogue of thermoluminescence. Nothing is destroyed or changed, and the process may be repeated. It was known as early as 1600, and is a property of most luminous sulfides. This may be one of the reasons that the afterglow of a sulfide which is handled will be shorter than that of one which is not handled, temperature and other conditions being the same.

**Class B-2, Electroluminescence.** A branch of electrophysical luminescence. A good example of true electroluminescence is found in gaseous conductors. When electric current is made to pass through a gas, the atoms will be ionized if the potential is high enough and if free electrons are present. Electrons are drawn toward the positive pole and they knock electrons from the atoms as they collide. The atoms minus the electrons have a positive charge and are drawn to the negative pole. This action is cumulative, and the path has a negative resistance. The light occurs not when the atoms disrupt but when the positive and negative ions recombine. This requires about  $\frac{1}{20,000}$  of a second in the case of neon and about  $\frac{1}{100,000}$  of a second in the case of mercury vapor which becomes a gas at elevated temperatures. The free electrons are always present, having been supplied by cosmic ray bombardment. A little argon is added which assists in starting because of its low ionization potential. A much lower percentage of the light lies in the visible spectrum than is the case with fluorescent solids. In the case of neon, there are bands in the infrared, and in the far ultraviolet there is a strong band as low as 740 Å. With mercury vapor the conditions are still worse in so far as visibility is concerned, except at very high pressures. The percentage of light radiated in the visible part of the spectrum increases with increase of current and pressure of its vapor, i.e., the wavelength of the emitted light increases with pressure. In the low pressure case there is more invisible light radiated than visible, until with further reduction in pressure we reach a point where about 0.3 ampere is passing through a tube having a diameter of one inch and about 75 per cent of the light falls in a narrow band centered around 2,537 Å.

Coat the inside of such a tube with synthetic fluorescent salts and the product is a fluorescent lamp, efficient because in the electroluminescent stage it is possible to make a gas radiate most of its energy at one wavelength, and in the second or fluorescent stage, because some fluorescent materials excited by 2,537 Å radiate the most of their light energy in the narrow band which embraces human vision.

It is also possible to induce phosphorescence in a gas by virtue of electronic bombardment. Molecular nitrogen in a discharge tube is converted through multiple collision processes to the atomic state, and, on further collision with metastable molecules, the molecules are brought into a higher excited level. On return to the normal state, a bluish white afterglow is noted which persists for sometime. This has been observed by the author and others in an ordinary nitrogen-filled lamp of large size by connecting it to a 100,000-volt high-frequency generator of the Tesla type.

**Class B-3, Due to Electrophysical Excitation.** This is a large group and includes the brightest sources of luminescence known.

*Class B-3-A, Positive Rays.* In electroluminescence, it was noted that the ionization of a gas by electric current gave rise to luminescence of the gas, producing a line spectrum. The impact of the positive ions themselves is capable of exciting fluorescence in solids, although the effects are weak compared to other forms of excitation. Natural minerals and synthetic materials show fluorescence by positive ions drawn from a hot oxide-coated filament to a negatively charged plate. In most cases the color of fluorescence with positive rays is the same as with cathode rays. Some materials, such as lithium chloride, were used in the early canal ray tubes in order to distinguish between the positive and negative particles. According to Trowbridge (41), lithium chloride fluoresced red with positive rays and blue with cathode rays. He also produced red fluorescence with cathode rays and claimed the difference in color was due to the difference in intensity of the exciting beams, but no mention was made of the temperature. The writer has observed that aluminum oxide activated with chromium and placed in a discharge tube glows blue at low vacuum and red at high vacuum. The gas pressure at low vacuum was such that cathode rays could not get through, owing to the short mean free path. It is significant that J. J. Thompson in his experiments on mass found that in helium the path of the cathode rays is marked by a bluish light whereas that of the positive rays is marked by a red glow.

The alkaline earth sulfides, under influence of positive rays, give a color similar to the high-temperature photoluminescence spectrum, proving that positive rays can excite a different luminescence from cathode or negative rays.

Alpha rays from a radioactive source are also capable of exciting luminescence. This is the basis of the so-called radium paints. Alpha rays are positive rays; in fact they are helium atoms which have lost two electrons. Zinc sulfide is the most suitable material for this activation. A few thousandths of a milligram of radium per gram of zinc sulfide will cause a steady glow without any other source of excitation. The half life of radium is 1,690 years. A higher radium content gives brighter fluorescence, but, if the content is too high, fluorescence is soon destroyed by the continuous bombardment of the active centers. Mesothorium, which has a half life of 7.9 years, has been generally used for economic reasons. The life is sufficient because zinc sulfide is sensitive to light and would be destroyed in this period of time even without any radioactive material. Mesothorium, however, is unobtainable at the present time and radium is used.

*Class B-3-B, Negative Rays.* The fluorescence excited in certain inorganic compounds, with and without heavy metal activators, by a beam of electrons is the brightest in the whole field of cold luminescence. The electron is the unit negative electric charge, which has been determined as  $-e = -4.80 \times 10^{-10}$  electrostatic units. It is 1,846 times lighter than the hydrogen atom. From measurements of the ratio of the charge to the mass of an electron, the mass is found to be  $9.01 \times 10^{28}$  grams. The mass of the electron is electrical in nature. Since modern theory recognizes the dualistic nature of matter, electrons can be considered as particles or as radiant energy. In the latter case they can have a wavelength assigned to them, which is convenient when considering Stokes's law, or calculating the electron paths in an electron microscope.

A discussion of wave mechanics does not come within the intended scope of this paper, but the theory is important in connection with energy studies in cathodoluminescence. Suffice it to say that the wavelength of a particle (any particle of matter) is found by dividing the quantum \* by the momentum of the particle. The velocity of an electron drawn towards a positively charged plate increases with the

\*The interchange of energy between matter and radiations occurs in discrete amounts called quanta. The radiant energy is expressed as  $h\nu$  for each quantum, where  $h$  is Planck's constant and  $\nu$  is the frequency.

voltage. It may be of interest to note that, according to theoretical equations developed by Lorentz on the basis of classical electrodynamic and (later) the Einstein theory of relativity, the mass of the electron increases with its velocity. Since the development of the hot cathode, however, most modern studies of cathodoluminescence are made at lower voltages than formerly. The tubes are usually sealed from the pump, and, because the variation of mass is inappreciable at velocities of less than 10,000 volts, this effect is not usually taken into consideration.

After a certain threshold voltage is reached, which is different for various substances, the intensity of fluorescent light increases proportionately with voltage, provided the beam current density is left constant. The threshold value is higher than can be accounted for theoretically, even with the limiting factor of space charge removed to a great extent by the hot cathode and conducting screens. The fluorescent effect is due to direct bombardment of electrons rather than to secondary emission electrons thought to occur in the case of X-radiation and by gamma rays.

Perhaps the brightest of all materials of this class is zinc sulfide activated with silver. The sulfides in general are very efficient but are also very sensitive, in that they break down easily under impact of the electron beam. Zinc orthosilicate activated with manganese is the classical example and is the most stable. Owing mainly to the fact that the spectral distribution of its light follows more closely than most materials the human eye visibility curve, it has figured in many experiments of historical importance, such as the range of alpha particles and the initial determinations of electron and proton mass. Many materials are excited by electrons which will respond to no other radiation. This is generally due to the fact that the percentage of impurities required is several thousand times greater than the permissible amount for visible or ultraviolet excitation, and these percentages were most often found in the natural minerals, once important in these studies. Today mineral luminescence is of interest only to the collector, and all commercial materials are made synthetically, in which process the activator and other factors are under complete control. As would be expected, materials which have a long afterglow in air have a very short afterglow in a vacuum. There are exceptions, however. Many materials, the uranyl salts for example, exhibit a different rate of decay with various types of excitation. Uranyl sulfate in air has an afterglow of 0.003 second when excited by ultraviolet, and in a gas at a pressure of a few millimeters of

mercury, an afterglow of 10 minutes when excited by cathode rays. A sample of calcite having an afterglow of only a fraction of a second at room temperature when excited by 2,537 Å radiation, might show an afterglow of an hour or more when excited by cathode rays at low gas pressure, and will glow still longer after excitation by Lenard rays in air.

The early workers with minerals were mainly concerned with the nature of fluorescence and the laws governing the emission of various spectroscopic bands at different temperatures and other variations, in order to work out a theory by which results could be predicted. At the present time the greatest interest lies in measuring and improving the efficiency of a given type. The first synthetics were of course based on chemical analysis of the most efficient materials reported by the early workers in this field (see Crookes [6]). It is now possible with a few guiding principles to predict in advance the approximate results to be obtained by creative formulation. Materials of all colors and many rates of decay can be made synthetically at the present time.

The stimulus for developing white cathode ray materials of high efficiency came about with two developments, both comparatively recent. They are television screens and cathode ray lamps. The cathode ray oscillograph tube developed by Braunn in 1897 made no special demands on the efficiency of the fluorescent salts. It appears that the first cathode ray lamps constructed for the express purpose of a source of light were Edison's, who demonstrated them at the Columbia Exposition in Chicago in 1893. He used calcium tungstate coated on the inside of a bulb which had a cold cathode and an anode of the same structure as in an X-ray tube, and operated these in a partial vacuum by a high voltage X-ray transformer. Although Edison thought that these lamps were operated by X-rays, we now know that excitation was caused by high-voltage cathode rays. The main difficulty with them was the high voltage required because of the cold cathode and the eventual cleanup of the residual air which acted as the ionized carrier. Had Edison carried on this work after Wehnelt invented the oxide-coated hot cathode in 1905, the history of lighting might have been different.

There is very little connection between Edison's fluorescent lamp and the present-day fluorescent lamp, which operates on a different principle, that of ultraviolet excitation. A lamp made by Andrews of the General Electric Company in 1912, operated by cathode rays just as Edison's, except that it was tubular instead of round and also re-

quired high voltage. Neither Andrews' nor Edison's lamp utilized mercury vapor.

There is no record of further improvement in cathode ray fluorescent lamps until the work of Schmidling (30, 34) appeared in 1934. He developed a vacuum lamp which eliminates the necessity of high voltage by using a hot cathode, one inch in diameter, the beam of which is controlled by an electron lens. Its efficiency is due in part to the fact that the same side of the large fluorescent target that is bombarded is utilized as the source of light. This lamp was also used as a television projection tube (31). It is the only type of fluorescent lamp free from stroboscopic effects.

The other device wherein efficiency is of great importance is the television receiving tube. It seems that the difficulties increase as the square of the increase in definition, and the light intensity available becomes less with each increase in scanning lines. About 1928 it began to be realized that the original ideas of Cambell-Swinton in England and of Boris Rosing in Russia for a cathode ray television system showed greater promise than the mechanical systems then in use. To date no single fluorescent material giving a white light of high efficiency has been found, and the screen of a television tube is composed of several salts. Two or more salts may be used, the main requirements being that they have the same rate of decay (after-glow) and that the combination gives a white or daylight effect. Each picture of course must disappear before the next "frame" appears.

In some cases when two salts crystallize in the same class, they may be mixed before heating. For example, zinc sulfide and cadmium sulfide both crystallize in the "wurtzite" or hexagonal form, and result in a homogeneous solid solution. This effect was first described by A. A. Guntz (9), in 1926. This may be done with several other combinations, the most important of which is zinc-beryllium orthosilicate. Although homogeneous crystallization will occur in all proportions, with resultant changes in the fluorescent color, a satisfactory white light has not yet been made in this way. It is necessary to mix two or more completed materials, the proportions of which may vary from batch to batch.

Owing to limitations of space, this subject can be treated only briefly, and these remarks are included only because they also apply in general to photoluminescence discussed farther on. In addition, it might be well to consider that the paint expert of the near future may find all pigments within his realm. He will no longer be painting with visible light alone but with invisible radiations of several types.

Since fluorescent materials are sources of light, not reflectors, color mixing is done by the additive process. The paint man is accustomed to the subtractive process, in which the primaries are blue-green, magenta, and yellow, the sum of which is black. When light sources are used, the primaries from which all other colors can be made are red, blue, and green, the sum of which is white. A fair white can be obtained by using any color in combination with its complementary. Examples are blue and yellow, magenta and green, and red and blue-green. When two colors are used to make white, purity of color would be detrimental. In fact it is possible only because the colors are not pure, and either one or both contain some of the other colors of the spectrum.

Most of us are familiar with the rudimentary principle of mixing colors or pigments, but, if an attempt were made to mix fluorescent materials on the basis of one's knowledge of colored pigments or dyes, the results would be very disappointing. As a good example, let us mix blue and yellow, which if done with colored pigments will give us green. Now blue and yellow colors do not actually make green. In the blue paint we have a mixture of blue and some green. The yellow paint contains yellow and some green. When mixed, the blue and yellow cancel each other out to make black, and the green remaining from each paint causes the final color to be green but less brilliant than either of the original colors. If pure blue light from a spectrum is mixed with pure yellow light from a spectrum, no green will be observed, but, instead, if the proportions are correct, will give a white light. Thus a mixture of blue and yellow paint pigments will give a green color, and a mixture of blue and yellow fluorescent pigments will give a white light. Another important difference is that in the latter case the sum of the two colors will be mixed with white, instead of with black as in the case of pigments. Satisfactory color matches are possible with fluorescent materials because most materials exhibit, within their range, a continuous spectrum. There is a large class of materials which give a line spectrum similar to gases, when a rare earth, samarium, terbium, etc., is used for the activators, but they are not used for this purpose. Other problems in connection with the television screen are not so simple, and it might not be out of place to mention them here.

The change of color during the decay period usually occurs in the first few hundredths of a second, in which time a large number of contrasts occur in the television image. The change in color is due to the fact that fluorescence and phosphorescence are characterized by

different bands in the spectrum, and the color is the total of all these. When the fluorescent bands die successively the color is the sum of the bands still radiating.

Another factor which complicates and affects the final color is that due to temperature. This is because the phosphorescent bands are quenched by light of longer wavelength than the emitted light, and, at the high intensities which television screens demand, a part of the accumulated energy is transferred to non-active molecules and is converted into heat. Now the phosphorescent band is usually of longer wavelength than the fluorescent band so that, if the former is partly quenched or dimmed, the color balance will be upset and the composite will be of colder hue as the temperature is raised (Schmidling [33]). This explains why fluorescent colors are more bluish when hot and more reddish when cold. There are many other effects too numerous to discuss in detail, such as dehanement by certain impurities which act in opposition to the activators or serve to inhibit fluorescence in general. Infrared quenching is not effective in cathodofluorescence. Modern screens are made conducting either by a light coating of metal applied to the surface or metallic conductors interspersed throughout the material. This is necessary because fluorescent materials are poor conductors and they quickly acquire an electric charge which tends to repel the electron beam. Maloff and Epstein (20) discuss behavior of the screen in relation to secondary emission of both the screen and its base.

**Class B-4. Electromagnetic Excitation.** *Class B-4-A, X-rays.* Many materials, organic and inorganic, which have only a short afterglow by ultraviolet excitation emit for a very long period when excited by X-rays. Calcite is an example. In fact one of the main problems in the manufacture of X-ray screens is the fact that the screen, used to intensify the photographic image, retains the image for a longer time than is convenient in a busy hospital. If the image is not removed, it will of course interfere with the next exposure. This has been overcome by introducing inhibitors which reduce the afterglow to a negligible value.

It is important to note that dehanement can be caused by other means than inhibiting metals. Levy & West use nickel (2 millionths of 1 per cent) and Shepard uses a halide salt. A large number of X-ray luminescent salts emit light in the near ultraviolet range as well as in the visible. A blue screen, usually calcium tungstate (whose fluorescence was discovered by Edison), is used in contact with the photographic film. A yellow or green screen is used for fluoroscopy or visual



examination. Zinc cadmium sulfide has replaced the historic barium platinocyanide for visual use. X-rays were discovered with the help of the last-named, coated on a piece of paper.

According to Hirschlaff (12), X-rays and gamma rays cause phosphorescence by secondary emission, rather than by the primary beam. For purposes of experiment, it may be mentioned that the gamma rays from radium may be separated from alpha and beta rays by a magnetic field. Since the gamma rays are not material particles, they will not be deflected. The alpha and beta rays will be deflected in opposite directions.

*Class B-4-B, Ultraviolet to Visible Light Excitation.* The largest number of all known fluorescent materials fall into this class. Substances excited by ultraviolet light include organic and inorganic compounds, pure and activated salts, gases, vapors, liquids, and solids. It is surprising that at this comparatively late date, with thousands of known materials on record, the useful applications are few in number.

Fluorescence by ultraviolet has been of great theoretical importance, especially in the simple compounds developed by Pohl and his collaborators (26). They worked with large crystals of pure alkali halides, which have no absorption bands in the visible range, until the metallic impurity is introduced.

From theoretical consideration, excitation by ultraviolet and visible light (or any other electromagnetic band) is inseparable and therefore it might be well first to give practical examples of each type before proceeding with the principles involved.

*Class B-4-B-1, Short Ultraviolet, 2,500 Å (Organic Materials).* There are relatively few materials in this class. In general, living material does not fluoresce in this range. Many of the acetates are unique in that they not only fluoresce in this range, but also show brilliant phosphorescence. An example is sodium acetate, which has a brilliant green afterglow after excitation by the 2,537 Å line emitted by mercury vapor.

*Class B-4-B-2, Short Ultraviolet, 2,500 Å (Pure Inorganic Materials).* Pure calcium tungstate fluoresces blue in this range and has a very short afterglow. Other materials of this class are the molybdates, platino salts, uranium salts, and salts of the rare earths.

*Class B-4-B-3, Short Ultraviolet, 2,500 Å (Impure Inorganic Materials).* When the above materials are activated by a heavy metal, the afterglow increases, as well as the brilliance. The tungstates are in general activated with lead, the silicates and borates with manganese.

One of the most useful materials of this class is zinc beryllium orthosilicate activated with manganese. This was originally developed in England. The tungstates and silicates are also sensitive to the very short wavelengths in neon at 740 Å. This makes it possible to use these materials in fluorescent lamps without the use of mercury vapor, which has a tendency to deposit on the fluorescent film and reduce the efficiency of the lamp. The blackening of fluorescent lamps caused by oxidation of this film (the oxygen is released from the fluorescent salt by reduction due to ultraviolet) has not yet been completely overcome. On the other hand, excitation by the 740 Å line in low-pressure neon, while having a lower initial brightness than the mercury vapor lamp, has almost perfect lumen maintenance for 10,000 hours. Tubes of this class, made by the author six years ago, are still in operation, the efficiency after the first 5,000 hours being greater than the initial efficiency.

When calcium tungstate is activated by samarium, the fluorescent color changes from blue to red and a line spectrum is emitted. The author has found that, when aluminum is used as an activator (5 per cent) in calcium and magnesium tungstate, the afterglow is greatly increased and helps to eliminate the stroboscopic effects in daylight fluorescent lamps.

Another series of activated compounds excited by short ultraviolet is peculiar in that an elevated temperature is necessary for fluorescence. These are the metallic oxides and carbonates. Some, such as aluminum oxide activated with chromium, will glow at room temperature, but are brighter at 100° C.

*Class B-4-B-4, Long Ultraviolet, 3,650 Å (Organic Materials).* This is the range in which almost all animal fluorescence, living and dead, is sensitive (not to be confused with animal chemiluminescence). There are many thousands of known examples. Outstanding ones are the organs of the human body, the hair, teeth, viscera. Human blood is fluorescent if the iron is removed. The B vitamin complexes can be separated by their fluorescence, and blood serum representative of several diseases has been found, by Reche, to glow with a characteristic color. Great care must be exercised in fluorescent analysis, and the method is useful only when all conditions are precisely specified. For example, the serum from a syphilitic patient gives a yellow fluorescence in a layer 1 mm. thick, and yellow-green in a layer 7 mm. thick, whereas the serum from gastritis shows yellow fluorescence at both thicknesses.

Fluorescence microscopy is of more immediate importance than macrofluorescent analysis, because in the former the usefulness does not depend so much on specific colors from specific materials, but rather on the additional differentiation obtained by natural fluorescence or by the use of fluorescent stains.

Some tissues, not ordinarily fluorescent, become so when stained with a fluorescent or even a non-fluorescent solution. This process, which will be important in the future, is called secondary fluorescence, and the materials are called fluorochromes. Berberine sulfate is fluorescent in the dry state, but when dissolved in water becomes non-fluorescent. If in this state, it is brought in contact with another non-fluorescent organic material, the combination immediately becomes fluorescent, even though wet.

TABLE OF FLUOROCHROMES (Haitinger)

Berberine sulfate	Rhodamine B extra
Chelidonium	Rhodamine 6 G
Chrysorupine	Thiazol yellow
Coriphosphine O	Thioflavine
Geranine G	Trypaflavine
Geranine S	Phosphine 3 R
Neutral red	Primuline yellow
Fluorescein	Esculin
Rosol red	

The chemiluminescent organs of insects, fish, etc., are all more or less fluorescent by long ultraviolet light. This appears to be more than coincidence.

Certain types of fluorescent paints are made from organic materials. Rhodamine B dye is not fluorescent in the concentrated dry state, but, when it is dissolved in a lacquer, it emits a brilliant orange-red fluorescence with an afterglow of only a few hundredths of a second. The afterglow is extended when introduced in a medium of high viscosity, such as sugar or gelatin. The lacquer-dye combination is the one used in stage work.

*Class B-4-B-5, Long Ultraviolet, 3,650 Å (Pure Inorganic Materials).* In general, pure inorganic materials exhibit only a dim fluorescence, if any, at this wavelength, but the exceptions, strangely, are among the brightest materials known. The best example is the large group of uranyl salts, which exhibit their brightest fluorescence when water of crystallization is present.

Whether or not pure zinc sulfide is fluorescent remains unanswerable because no one has been able to purify this material to the point

at which no fluorescence occurs. Theoretically it should be non-fluorescent if perfectly dry.

*Class B-4-B-6, Long Ultraviolet, 3,650 Å (Impure Inorganic Materials).* It is difficult to find light-colored inorganic materials which do not show some fluorescence by long ultraviolet light. Among the materials especially made for this excitation are zinc and zinc-cadmium sulfides activated by copper, silver, bismuth, and manganese. In general, the length of afterglow decreases and the brightness increases, with increasing percentage of impurity.

A new art is being developed in the analysis of ordinary materials of commerce, such as chemicals, drugs, and paints, by their fluorescent color under long ultraviolet light supplied by a high-pressure mercury vapor lamp and a Wood's glass filter. Most of the initial work was done by Haitinger, completely described in English with additions of their own by Radley and Grant (27). This combination has also been used in the examination of paintings and other works of art. A new addition or repair of an alabaster or marble figure will give very slight or no fluorescence, whereas the older parts will glow brilliantly (28).

*Class B-4-B-7, Excitation by Visible Light (Organic Materials).* Many of the materials which are excited by long wave ultraviolet also respond to the shorter rays of visible light. This is especially true of organic materials. The "bloom" on the surface of oil, for example, is caused by absorption of visible light of shorter wavelength than the emitted color. The sodium salt of fluorescein is so efficient in this respect that it has been used to trace the course of underground streams. The fluorescent color is yellow-green, and a few milligrams in a gallon of water is sufficient to cause a brilliant fluorescence by visible light (blue) after all ultraviolet light is removed by filters. The effect is enhanced by alkaline solution and quenched by acids.

*Class B-4-B-8, Excitation by Visible Light (Pure Inorganic Materials).* These are mainly materials whose range is so great that the excitation extends into visible wavelengths, even though their greatest sensitivity lies in the ultraviolet range. We shall again consider the uranium compounds. Uranium oxide and uranium sulfate are both highly fluorescent by short ultraviolet. But when visible light is used as the exciting source, the oxide is no longer fluorescent, the activity being confined to those materials in which water is present.

*Class B-4-B-9, Excitation by Visible Light (Impure Inorganic Materials).* Most of the complex sulfides of zinc and of the alkaline earth metals when suitably prepared have one or more excitation

bands situated in the visible region. The exciting wavelengths extend farther into the visible with increasing molecular weight of the solvent (sulfide), for example barium sulfide activated with bismuth.

### FLUORESCENT PRINCIPLES

The study of fluorescence is at the present time more an art than a science. The guiding principles have been arrived at empirically, and the laws by which one can predict results are few indeed. Even these have been revised from time to time. Therefore, in this short presentation we shall not hesitate to mix theory and practice, which are so dependent on one another. We shall be especially concerned with the long afterglow materials because of their wartime interest and usefulness, and specifically with the sulfides of section B-4-B-9 (page 683).

Stokes's law, which states that the fluorescent light is always of longer wavelength than the exciting light, has always been the center of interest as well as controversy. There are many claims in the literature of cases which invalidate this law, but it appears that these divergences are unreal and result from a misapplication of the law. This law was revised by R. W. Wood (44) to read as follows:

The "center of gravity" of the complete fluorescent band is always of greater wavelength than the excitation band, the latter term meaning a superposition on the absorption spectrum of the energy curve of the exciting light. . . . The exceptions to Stokes's law occur when the atom or molecule possesses energy of vibration at the time of its excitation to a higher energy state, the return transition carrying it to a lower state than the original one, resulting in the emission of a frequency higher than that of the exciting radiation.

The exceptions are more marked in vapors. This revision was based mainly on the work of Nichols and Merritt (5, 24), who summarized Stokes's law as follows:

If we isolate a single band of the luminescence spectrum it is found that the distribution of intensity throughout the band is independent of the intensity and wavelength of the exciting light.

During the decay of phosphorescence each band of the luminescence spectrum behaves as a unit, i.e., the wavelength of maximum intensity and the relative distribution of intensity throughout the band remain unchanged.

What is usually observed, therefore, is that the intensity of the individual bands may vary with different wavelengths of excitation. Also, in a complex sulfide, the individual bands may, and usually do,

have different rates of decay. These last two factors are responsible for the difference in the total fluorescent color when excited by various sources and for the change of color which some materials undergo during decay.

The conclusion is that Stokes's law is always obeyed for fluorescence. If the exciting line is situated inside the emission band only the part of the band of longer wavelength than the exciting line is emitted, but during phosphorescence the full emission band will be produced.

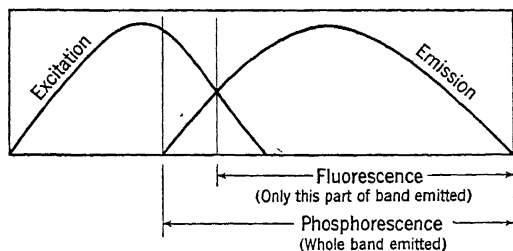


FIG. 5. Anti-Stokes's Emission.

(See Fig. 5.) The extra energy is provided by the thermal motion of the surrounding medium. Stokes's law therefore can be violated for phosphorescence, but not for fluorescence.

## ACTIVATION

The alkaline earth sulfides, activated with heavy metals and dispersed in solid solution by a flux, exhibit the longest afterglow. The base material, usually called the solvent, is composed of calcium, barium, strontium, or zinc sulfide. The activators most often used are copper, zinc, bismuth, manganese, and silver. The flux is usually a sodium salt or combination of salts. In the case of zinc sulfide, the fluorescent color depends on the activator; it is green with copper, blue with silver, green with bismuth, yellow with manganese, and light blue with gold. As stated in the section on cathode ray excitation, the fluorescent color of zinc sulfide can also be changed by replacing a part of the zinc with cadmium. In the case of copper activator, the color can be changed from green to red by increasing the cadmium sulfide content from 10 to 80 per cent. The best percentage of activator varies with each one, but with copper the best results are obtained with 0.0001 gram of copper for each gram of zinc sulfide.

In the case of the alkaline earths, let us consider strontium sulfide for comparison. Here 0.00006 per cent of copper is used for each gram

of strontium sulfide, and the color, with calcium fluoride as the flux (0.04 gram), is greenish blue.

With the alkaline earth sulfides, the color of a given sulfide can be changed by the flux; but this effect, in turn, depends on the activator used. When bismuth, zinc, or manganese is the activator, the color of phosphorescence is not changed by the flux. But when copper and lead are the activators, the phosphorescent color depends on the flux. The color in some instances also depends on the temperature of calcination which is usually in the range of 800 to 1,100° C.

Treated as a group, the color of the alkaline earth sulfides shifts to longer wavelengths with increase of dielectric constant of the solvent. The wavelength of the exciting bands increases accordingly. Thus, when bismuth is the activator, the phosphorescent color of calcium sulfide will be violet, strontium sulfide will be blue-green, and barium sulfide will be orange. The afterglow in each will be of longer wavelength than the fluorescent color. The absorption of the exciting ray is greatest for those wavelengths which produce the strongest afterglow. Therefore, since the absorption is greatest at the shorter wavelengths (least transmission), the strongest phosphorescence is usually produced by the shorter wavelengths and the longest afterglow by the longer wavelengths. Excitation, of course, may occur in one, two, or more bands. Since the fluorescent light is quenched by light of longer wavelength than the emitted light, the total effect of excitation of an alkaline earth sulfide by a source such as a foto-flood lamp is very complicated. Some wavelengths are exciting the material; others are quenching it.

### Electron Theory of Fluorescence

Let us examine the case of strontium sulfide activated with bismuth.

There is one absorption band located at about 3,200 Å and another in the visible range at about 4,360 Å. The emission in blue-green is peaked at about 5,070 Å.

When exposed to the exciting source, the energy of the absorbed radiation knocks an electron from the parent atom. The crystal lattice contains many distortions or cracks, and the electron is trapped in one of these "electron holes,"\* in a stable or metastable position. The intensity and duration of phosphorescence depend on how long it takes the electron to return to ground level. Its return is accompanied by

\* An "electron hole" may be visualized as an electron occupying a space in the lattice where a negative ion should be.

the liberation of a photon of light of lower energy (longer wavelength) than that of the exciting light. The difference in energy is absorbed as heat. If the electron returns to the same parent complex, the decay of phosphorescence shows an exponential curve, in which case there is no photoconductivity. But this rarely happens, and the decay curve is only approximately exponential. In the case of phosphorescence, the electron moves far enough away from the excited

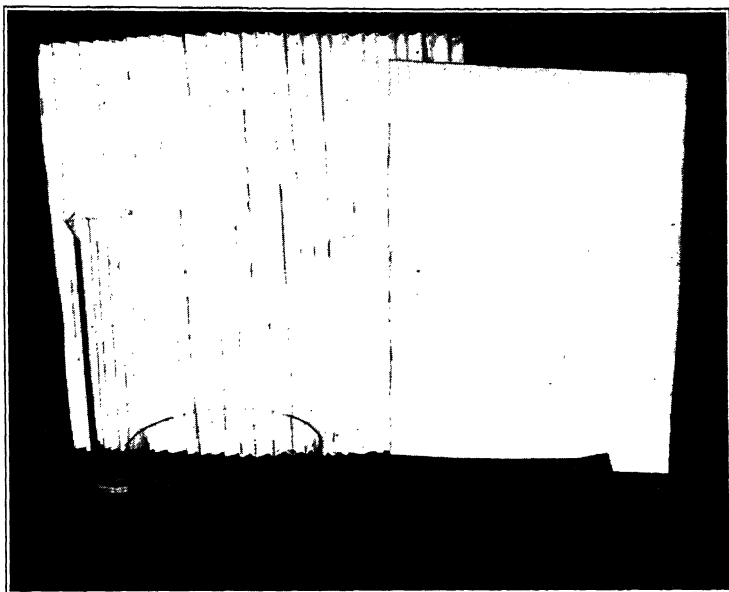


FIG. 6. Relative brightness showing brightness of corrugated luminous sheet compared to flat luminous sheet. Both have same type luminous powder, and are from the same batch. Both in polystyrene. Exposure 2 minutes, by their own light only—F 16 at 3 feet, SS,XX pan. film.

atomic center (proved by photoconductivity) to be loosely held by the medium. The return is delayed by the temperature and viscosity of the "surround." It can be stopped completely by freezing. The return can occur only if thermal energy is taken up from the surrounding medium. The time-decay curve is also lengthened by self-excitation. If the phosphorescent light happens to fall inside an absorption band due to a different unexcited center, resonance occurs, and the second atom is then excited to a higher energy level, from which a return may be made to the ground state or a lower metastable condition with emission of phosphorescent light. Figure 6 shows the added bright-



ness obtainable by self-activation. The corrugated sheet and the plane sheet were both exposed at the same time. In the case of  $\text{SrS:Bi}$  \* self-activation occurs because a part of the blue-green emission, although peaked at 5,070 Å, extends to a shorter wavelength than the maximum excitation at 4,360 Å. At high temperature the electron is released more easily, and the afterglow is shorter but more intense, the same total amount of light being emitted. This acceleration may be purposely caused by infrared. If near infrared, red, or indeed any light of longer wavelength than the phosphorescent light is present, the phosphorescence will be dimmed in proportion to its intensity. The author has found it advantageous in the case of luminous plastics, such as polystyrene and methyl methacrylates, impregnated with strontium sulfide, to include a blue-green dye which permits the exciting radiations to penetrate but prevents the quenching by longer wavelengths than green. It has been shown by Lenard and Pohl that phosphorescence is connected with photoelectric processes. An increase of conductivity is observed when the material is excited between the plates of a condenser. The increase is greater when the exciting light corresponds to the most sensitive input bands of the material.

The purpose of the search for a photoelectric process in these materials is of course to find proof that there is a connection between the absorption of light by the active centers and the emission and displacement of electrons in the medium. From this point on, the action becomes a little obscure and the exact mechanism involved in the various transformations of energy is still unknown. It is important to note that, in practice, these materials exhibit hysteresis, i.e., the intensity of afterglow depends upon their previous history. Excitation and decay should occur at least a dozen times before taking measurements. The phosphorescent sulfides are affected by sound, heat, light, touch, acid, and shock. They can therefore be said to have a sense of memory, feeling, hearing, and smell.

We are now in position more or less to complete the picture of activation. The base materials must be the purest obtainable so that the activation in the small amounts mentioned will be effective. Iron has the greatest inhibiting effect, but the presence of other metals will, in general, also inhibit the effect of the intended activator (this is not true of the rare earths). Assuming a pure solvent and the optimum percentage of activator, we see that an increase in this amount

\* Chemical term in general use for designating the base and activator of the luminous compound.

will cause greater initial brilliance but shorter afterglow, and a smaller amount of activator will result in a lower initial intensity with a correspondingly longer afterglow, for visible light excitation. For ultraviolet excitation of fluorescence, when phosphorescence is not desired, the percentage of activator is increased by about ten times. For cathode ray excitation the percentage is often as much as 0.5 or 1.0 per cent.

Zinc sulfide has, in general, a brighter though shorter afterglow than the alkaline earth sulfides.

### EXCITATION AND EMISSION

A material, designed for excitation by visible light, as strontium sulfide, can be excited by invisible ultraviolet light. If the intensity is high enough, all bands (for phosphorescence) will be excited; but it usually happens that the initial intensity is not so high as with photo-flood excitation, and after several hours have elapsed the intensity is about the same. If a photo-flood lamp or any hot source is used, care must be exercised to excite the material at a distance of at least six feet to prevent undue heating of the sample. Since the intensity of afterglow is a function of temperature, the light can be extinguished after excitation by freezing. Phosphorescence will again occur in the sample on return to room temperature. Also, since only a part of the light stored is emitted at room temperature, the remainder will be emitted by an increase in temperature. The ideal excitation is therefore a cold source composed of all the necessary wavelengths for excitation. Clear, north skyshine comes closest to this ideal, but is not perfect, because the shorter wavelengths are not present.

In simple compounds the rate of decay, in most cases, follows an exponential curve. But in the complex sulfides in which a number of absorption and emission processes occur at the same time, and independent of one another, a measurement of the decay of phosphorescence with time will not show an exponential curve. Apart from the apparatus used to make this measurement, there are two ways in which the results can be recorded. One is to measure the length of time required for the light to decay to a definite intensity; the other is to measure the actual or relative intensity at given intervals of time. Each method has certain advantages. The first is recommended by the British Government as the most suitable method for testing materials used in A.R.P.\* work. It gives the kind of infor-

\* Designation for Air Raid Precautions.

mation that the user would want. However, since it gives no information on the shape of the decay curve, and for the other reasons discussed under measurements, the second method is most suitable for research and manufacture. The color as well as the decay curve changes at elevated or reduced temperatures. Therefore the decay curve is meaningless without a statement of temperature.

### PARTICLE SIZE

The intensity and length of afterglow increase with increase in particle size. Phosphorescent powders undergo both physical and chemical change when crushed, and it is the aim of manufacturers to do as little crushing as possible in production. A fair estimate of the average particle size, after sieving, can be made under the microscope.

A little of the powder is stirred in Canada balsam more diluted than usual with xylol. A drop of this mixture is transferred to a thin slide, a cover glass applied with less than usual pressure and ringed with gold size or shellac. The light source is adjusted for critical illumination, i.e., the image of the light source is focused in the field. The top lens of the eyepiece is now removed, and a circular eyepiece micrometer is laid on the diaphragm opening and the lens replaced. The prepared slide is now removed and replaced with a stage micrometer with which the eyepiece is calibrated. This must be done with the objective which will be used for the measurements, in this case, 4 mm.-40x and a 10x eyepiece. Remove the stage micrometer and insert the slide. Place a dark-field disk in the filter holder beneath the substage condenser, and the opaque part of the disk for a 4-mm. objective should be about 16 to 18 mm. in diameter. This depends, however, on the instrument and must be found by trial. The particles will now stand out with great contrast and brilliance upon a black field, as though shining by their own light. The method is far superior to the usual transparent field, for this purpose. Exact measurements of an individual particle may be made with a filar micrometer. For further information on this subject, the reader is referred to Gage's (7) book on *The Microscope*.

### OTHER FLUORESCENT PHENOMENA

There are numerous other fluorescent effects, of theoretical importance and outside the scope of this short résumé, a few of which should be called to the attention of the beginner or student of this

fascinating subject. Polarized fluorescent light is emitted by certain solutions and even crystals (44).

The fluorescence of chlorophyll is interesting because of its importance in the respiratory process of plants (12). The fluorescence of gems and minerals is important when studied quantitatively, especially with the help of an ultraviolet monochromator. In this way the characteristics of many natural materials were uncovered and duplicated synthetically. The whole subject of fluorescence is on the threshold of great importance to the medical scientist. There is reason to believe that the slow progress in the art of luminescence since 1602 parallels the history of the microscope. In both fields, the workers were so impressed by the sheer beauty of the phenomena under observation that they became the slaves of the instrument instead of its master. This view, in the case of the microscope, has recently been admitted by medical researchers. The quicker we forget about large collections of beautiful fluorescent minerals, fluorescent fireplaces, fluorescent caves, and what-not (Sutter fluorescent show—4 tons, Murdock fluorescent cave, unlabeled public museum exhibits), the greater will be the probability of utilizing this tool for the benefit of mankind. Casciarola did not find gold on that historic Sunday evening stroll on the slopes of Monte Paterno; he found something far more valuable, the social importance of which is just now beginning to be realized. Progress will be parallel to the development and use of new instruments designed for the purpose. It is interesting to note, in this connection, one more type of fluorescence, recently discovered, in which, after irradiation by X-rays, a high enough emission occurred in the short ultraviolet (fluorescence) to kill bacteria deeply imbedded in tissue.

### DEMONSTRATIVE FORMULAS

Methods of preparation will now be given for studying the fluorescence of each of the foregoing examples. Since the literature is full of discrepancies and omissions, only formulas found by personal experience to be correct will be given. By making each of these preparations, the student will have, for further study, an example of all the known classes of fluorescence.

#### Permanent Chemical Change

**Class A-1-A, Inorganic Luminescence, Non-living.** Drop a piece of phosphorus (care!) the size of a pea into a bottle containing 200 cc.

of previously boiled and cooled olive oil. Whenever the stopper is momentarily removed, oxygen will enter. The glow will last for several hours with each charge of air.

**Class A-1-B, Organic Luminescence, Non-living.** *Solution 1.* Dissolve 5 grams of sodium hydroxide in 500 cc. of water. Add 2 grams of luminol (not luminal) and shake until dissolved. *Solution 2.* Dissolve 2 grams of potassium ferriocyanide in 500 cc. of water, add 5 cc. of ordinary 3 per cent hydrogen peroxide solution. Mix small quantities of each in a darkened room, and the solution will emit enough blue light by which one may read.

**Class A-1-C, Organic Luminescence, Living.**

*Culture Medium for Luminous Bacteria*

1.5 grams agar jelly.	1 gram calcium carbonate.
2 grams peptone.	95 cc. sea water.
1 cc. glycerol.	

Store this solidified medium in sterile jars. When ready for the experiment, inoculate with natural sea water in a petri dish. Scrape off the growth and suspend in sea water. Shake the solution to make it absorb oxygen. The bacteria will glow brightly; also catch a firefly. The season, as well as the type caught, will vary in different localities. Use an anesthetic and dissect the luminous organ. If not crushed, this organ, even after drying, will glow upon addition of aerated water. It is also fluorescent.

**Class A-1-D, Crystalloluminescence.** Crystallize potassium sulfate in the dark.

**Class A-2-A, Triboluminescence, Type A (Pure Material).** Shake uranium nitrate crystals in a glass jar, in a very dark room.

**Class A-2-B, Impure Material.**

Zinc oxide CP	50	grams
Flowers of sulfur	50	grams
Manganese dioxide	0.01	gram

Mix thoroughly in alcohol. Evaporate. Heat in a porcelain crucible at 900° C. for 30 minutes. The material will glow when struck, ground, or scraped, without previous excitation, and will eventually lose this property.

**Class A-3-A, Electrophysical Bombardment.** Seal a few tablets of potassium bromide in a glass tube, closed at one end and having a constriction at the other. Seal to a vacuum pump and exhaust to 2 or

3 microns. Admit argon to a pressure of 2 mm. Cathode rays can be generated by application of the high-frequency spark from the outside. It is not necessary to build a hot cathode tube and the above quick method will illustrate the point very well; the fluorescence will be blue and after a few moments the chemical will turn dark blue and finally black. On opening the tube, the white natural color can be restored by gentle heating.

**Class A-3-B, Lyoluminescence (Pure Materials).** Expose crystals of lithium sulfate to cathode rays until they are discolored. Break open the tube and dissolve the sulfate in water, and a fluorescent glow will be seen in the dark.

**Class A-3-C, Impure Material.** Activate 100 grams of aluminum oxide with 0.01 gram of chromium oxide. Heat at a temperature of 700° C. for 15 minutes. Excite by cathode rays until chemical reduction is complete. The strong red glow will decrease almost to zero. Decrease the argon pressure and increase the electron velocity. A bright light will build up (candoluminescence) but the color will be white. Use about 2,500 volts, direct current, and a hot cathode for best results, but the high-frequency spark and cold ampoule will also work.

**Class A-4.** Expose ordinary bottle glass to X-rays for 3 hours. The manganese usually present will act as an activator, and the clear glass will turn to a beautiful amethyst color. Place a number of pieces of clear bottle glass on a roof and leave exposed for several months for the same result, or expose crystals of Kunzite to ultraviolet light or X-rays and the color changes can be observed in shorter time. The color changes in reverse will occur upon heating the crystal.

### **Temporary Chemical Change. Physical Luminescence**

**Class B-1, Triboluminescence, Type B.** Expose luminous zinc sulfide hereinafter described, to ultraviolet, and measure the time of complete decay at room temperature. Expose it again and agitate it gently in a mortar. The decay time will be shorter. Expose it again and allow it to decay naturally. When it is completely dark, agitate it in a mortar and the residual phosphorescence will be emitted.

**Class B-2, Electroluminescence.** Break the tip of an older type of 3-electrode radio tube and, after sealing on a new exhaust tube, seal it to a vacuum system. After it is baked, allow the tube to cool and admit neon to a pressure of 10 mm. The ionization potential can be measured in this way, and fluorescence of gas atoms can be shown.

Insert a high resistance in the plate circuit to control the negative resistance of the gas. If a quartz tube a foot long and 10 mm. in diameter is used instead of the radio tube, a few millimeters pressure of argon and a drop of mercury can be introduced, the latter by distillation from an appendage. Use iron shell electrodes and about 2,000 volts alternating current. With this set-up, the increase of wavelength in the spectrum can be shown to occur with increase in current. When the current is reduced to a few milliamperes, zinc orthosilicate and calcium tungstate will glow intensely, without a filter, by excitation from the 2,537 Å line, but will cease to glow at high currents when the output is high in the 3,650 Å region. An ultraviolet filter is needed in the latter case to screen out the visible light.

**Class B-3-A, Positive Rays.** Insert a compressed lump of lithium chloride in the center of a clear glass discharge tube about 0.5 inch in diameter and after evacuation admit a few millimeters of argon. Excite with high-voltage direct current or partially rectified alternating current, which is simpler. A large spark coil will suffice. The part of the salt which faces the negative electrode will fluoresce blue and the part which faces positive will fluoresce red. The gas pressure must be adjusted for best results.

**Class B-3-B, Negative Rays (Synthetic Zinc Orthosilicate).**

Zinc oxide CP	65	grams ZnO
Silicic acid CP	62.4	grams $\text{H}_2\text{SiO}_3$
Manganese chloride CP	6	grams $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$

Dissolve the chloride, mix all together thoroughly, and evaporate to dryness. Place in a pebble mill, add alcohol, and grind for 24 hours. After drying and sieving, place in quartz crucible and heat to 2,250° F. for 3 hours. Sieve. Fluorescence is brilliant yellow-green when excited by an electron beam, cathode rays, X-rays, or by the 2,537 Å line from mercury vapor. Use more activator for electron beam excitation than for ultraviolet.

**Class B-4-A, Electromagnetic Excitation X-rays.** Heat CP calcium tungstate at a temperature of 982° C. and pour into water. Filter, evaporate to dryness. Fluorescence by X-rays will be blue and brilliant. No activator is purposely introduced.

**Class B-4-B-1, Short Ultraviolet (Organic).** Expose sodium acetate to 2,537 Å line from a cold quartz lamp operating at a low current density (25 ma. for 10-mm. tube). It will show green fluorescence and phosphorescence.

**Class B-4-B-2, Pure Inorganic Material.** Expose the calcium tungstate of B4-A or barium platinoeyanide or potassium uranyl sulfate to 2,537 Å. The fluorescence will be blue, blue-green, and yellow-green, respectively.

**Class B-4-B-3, Impure Inorganic Material (Zinc-Beryllium Orthosilicate).**

CP Beryllium oxide	100	grams BeO
CP Zinc oxide	325	grams ZnO
CP Silicic acid	312	grams $\text{H}_2\text{SiO}_3$
CP Manganese nitrate	62.1	cc. of 50% solution of $\text{Mn}(\text{NO}_3)_2$

Mix the paste thoroughly with water; evaporate. Grind in pebble mill with alcohol for 24 hours. After drying and sieving, heat in quartz crucible for 1 hour at 2,050° F. Cool quickly by dumping hot crucible on a quartz plate. Sieve. The fluorescence by 2,537 Å will be yellow-orange. Make a binder solution by dissolving collodion cotton in amyl acetate, equal parts by weight. The solution is best made by rolling the ingredients overnight in a pebble mill. Thin with amyl acetate and add a few drops of dibutyl phthalate to each 100 cc. Stir in enough powder to make a thin paint and pour into a glass tube an inch or so in diameter. On pouring it out, a thin film will adhere to the glass. Drive off the binder by heating the tube with a bunsen flame while passing a slow stream of air through the tube. Seal in electrodes, either hot or cold cathodes, and exhaust as usual with heat. Drive the gas out of the electrodes by either internal or external bombardment, depending on the type of electrodes used. When cool, distill a pinhead of mercury in the tube and add argon to a pressure, depending on the diameter and type of tube. The product is a daylight fluorescent lamp. If operated at a current of about 300 ma. for a tube 1 inch in diameter, the greater percentage of the emission of the mercury vapor discharge will be at 2,537 Å. The yellow-orange fluorescence excited thereby mixes with the visible light from the mercury vapor by the additive process described earlier, and the total color is white.

**Class B-4-B-4, Long Ultraviolet, 3,650 Range (Pure Organic Material).** Dissolve 0.1 gram of rhodamine B extra in 10 cc. of alcohol and add this to 1 quart of pale white shellac. Paint this on paper, cloth, wood, etc. Excite by a small argon lamp, or better a mercury vapor lamp with a corning No. 586 ultraviolet filter. This is a glass filter colored with nickel and cobalt oxide.



An invisible fluorescent paint can be made by dissolving anthracene in benzol and adding a little rubber cement as an adhesive. The fluorescence is blue with CP anthracene and green with the technical grade. The fluorescence is very bright but less permanent than the dyes. Other dyes which become fluorescent in solution are rhodamine 6A—yellow; eosin—red; and auromine O—yellow. The fluorescence of most other dyestuffs is more dependent, both in color and intensity, upon the base in which the dye is impregnated. Examine the teeth, hair, and fingernails at this wavelength. When you look at the lamp the whole room will seem to you to be filled with a violet haze. This is due to the fluorescence of the eyeball and the film in front of it.

**Class B-4-B-5, Pure Inorganic Materials.** Expose uranyl potassium sulfate to the lamp.

The afterglow is yellow-green and persists for 0.03 second.

**Class B-4-B-6, Impure Inorganic Materials.** Dissolve 0.01 gram of uranine in 500 cc. of water. A few grams of boric acid are wetted with this solution, stirred well, and evaporated. The material in this state is brilliantly fluorescent but not phosphorescent. It is now heated to the melting point in a porcelain crucible and cooled. The afterglow is now so brilliant after exposure that it can be seen in daylight. The color is blue-green. Other colors can be made in the same way with rhodamine B and 6A, but more dye is necessary.

**Class B-4-B-7, Excitation by Visible Light (Organic Material).** Dissolve 1 gram of quinine sulfate in weak sulfuric acid solution. Examine in daylight. Observe the surface at a small angle just below eye level. The fluorescence is blue. Also examine the extract from the bark of the chestnut tree, by macerating in hot water. The blue-green fluorescence is due to esculin. Examine the uranine solution in daylight.

**Class B-4-B-8, Pure Inorganic Materials.** Examine uranyl nitrate crystals in daylight through colored filter glasses, or at night time by exposure to a blue bulb. Convert to, or examine, sample of uranium oxide. The fluorescence is lost due to the lack of water of crystallization.

**Class B-4-B-9, Impure Inorganic Materials (Zinc Sulfide).**

Pure zinc sulfide	10	grams ZnS
Pure nitrate (as copper)	0.001	gram, $\text{Cu}(\text{NO}_3)_2$
Sodium chloride	0.3	gram NaCl
Magnesium fluoride	0.3	gram $\text{MgF}_2$

Dissolve zinc chloride in HCl and run hydrogen sulfide gas into the solution. Collect the first precipitate by filtration. Then the solution is supersaturated with ammonia. Precipitate the iron and heavy metals with ammonium and sodium sulfide. After precipitation and filtering, the zinc sulfide is best precipitated slowly by hydrogen sulfide. It is then filtered and dried and mixed with the fluxes. The activator  $[\text{Cu}(\text{NO}_3)_2]$  is added as an alcoholic solution and dried,, ground fine, and heated at a temperature of  $1,093^\circ \text{C.}$ , the length of time depending on the amount heated. On cooling it is washed in water to remove the fluxes. The heating should be done in a platinum crucible. If the  $\text{MgF}_2$  is omitted, the powder will be softer, the afterglow not as long, but it will be brighter.

### Demonstration of Thermophosphorescence

After excitation of the above material, allow the light to decay naturally by placing overnight in a closed box. Then heat the material to  $93^\circ \text{C.}$ , when the residual phosphorescence will be emitted.

### Quenching

Excite the material with daylight as before. Cover one-half with black paper and expose the other half to a red light. The quenching effect occurs immediately.

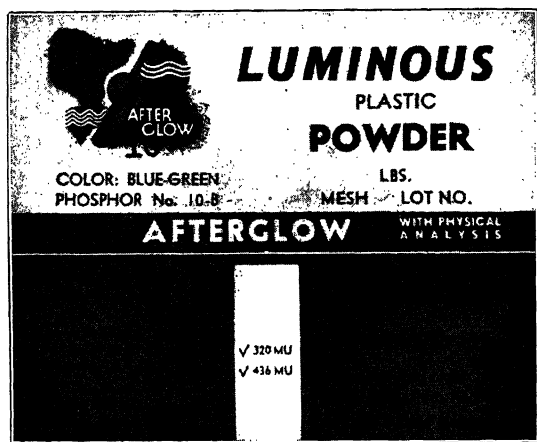
### Freezing

Excite as before. Pour liquid air over sample. The light will go out immediately and will begin to glow again on return to room temperature. For the opposite effect drop a cake of paraffin wax into liquid air and expose to long ultraviolet light. At this temperature a long bright afterglow will be observed which is lost upon return to room temperature.

## VEHICLES FOR LUMINOUS PAINTS

Considerable advance has been made in recent years in the formulation of vehicles for the alkaline earth sulfides. Many a pound of good luminous powder has, in the past, been spoiled by the vehicle, and it is quite probable that the failure to find any more important uses for this class of products than in mere novelties can be ascribed to this one cause. The author is fortunate in having samples of Lenard sulfides sealed in glass tubes which are about thirty years old. Deterioration has been slight, and, while they were not as good as

present-day materials, they do show what the possibilities have been. Zinc sulfide of course has never been a problem in this respect.  $\text{ZnO}$  is a stable and insoluble compound, and the luminous  $\text{ZnS}$  by the best modes of manufacture in which the fluxes are removed by a sludging process are relatively pure. Their main defect, in point of stability, is that the emissive centers are destroyed by light (also by physical bombardment of alpha rays and cathode rays, as evidence that it is the emissive centers that are destroyed). Many types of vehicle can be used with zinc sulfide, even the oils, provided they are not too acid.



*Courtesy of the Fluorescent Pigments Corporation*

FIG. 7. Label Showing the Physical Analysis of a Luminescent Material.

The alkaline earth sulfides, on the other hand, are very sensitive to both moisture and acid and are easily ruined. Strontium sulfide is the worst offender in this respect and is the most difficult in general for which to formulate a vehicle. Barium sulfide is also sensitive, but calcium sulfide is not especially difficult to work with. The reason for this is interesting, and appears to be due to the fact that not all the calcium present has been converted to sulfide but about 25 per cent appears as sulfate. A pure form consisting of only sulfide has been prepared and found to be highly unstable. For this reason a hybrid form is manufactured which contains both calcium and strontium sulfides. It has some of the best qualities of each in that it has the stability of calcium sulfide and the long afterglow of strontium. It is not so bright as the latter however.

Advance in formulation has been in two directions. First, there is the use of modern plastic resins, unavailable to the earlier workers.

Second, there is the use of neutralizers or acid acceptors. Continuous production of acid is more harmful than a slight original acidity that can be neutralized.

No metallic driers are used and the paint dries by solvent evaporation. Because of the rapid deterioration which occurs when foreign metals enter the crystal lattice, the pigment and vehicle are no longer supplied in separate compartments of the same container; but in the best practice the paint is furnished ready mixed in brown glass bottles. One manufacturer, the Fluorescent Pigments Corporation, has for several years furnished the physical analysis on the label.

It is hoped that eventually others will also adopt this procedure, not only because it makes the manufacturer responsible for the consistency of the product (one of the most desirable qualities) but also because this practice tends to remove luminous paints from the toy class into a scientific field. The label gives information pertaining to the peak wavelengths of the excitation as well as the emission band, the exciting source for which the material was designed, the length of afterglow as a function of temperature, and other pertinent information which will permit the user to predict results with a given type of material in connection with his own product.

## REQUIREMENT FOR A VEHICLE

### Ultraviolet Transmission

Since the initial brightness depends on excitation of all spectral bands, it is important that the vehicle transmit as high a percentage as possible of ultraviolet light. The ideal vehicle would transmit a high percentage at 2,200 Å but this has not yet been attained in practice. The plasticizer is usually the most opaque component. To test for ultraviolet transmission, apply a thick film on a slip of ultraviolet transmitting glass and support it below the ultraviolet source, or it may rest directly on the meter. A satisfactory and inexpensive meter sensitive to ultraviolet is easily prepared by cutting a slip of ultraviolet transmitting glass to fit into the window depression of a pocket foot-candle meter of the photoelectric type, such as the Weston. The type used for calculating photographic exposure is also suitable. The slip is coated on the underside with a yellow-green fluorescent material, to which color these meters are most sensitive. Potassium uranyl sulfate is excellent. The fluorescent light is proportional to the intensity of ultraviolet light when the visible light is filtered out. If the source is a mercury vapor lamp, some minutes must elap

come to a stable condition, and it is advisable to have an ammeter in the circuit with some means of control. A reading is made by noting the deflection on the foot-candle meter, through the film of vehicle, and subtracting it from the reading obtained through the uncoated half of the slip. This procedure is much more reliable than a visual evaluation; besides it gives a definite quantitative (or semi-quantitative) result that may be recorded. It is interesting to note that, since a vehicle obviously cannot absorb what it transmits, and only that which it absorbs can cause chemical change, it should be possible to predict future discoloration of the vehicle on the basis of its ultraviolet transmission or absorption.

Only materials which are water-white (colorless) are useful.

### SOLVENTS

The best solvents are the neutral cyclic or paraffin hydrocarbons. Xylol and toluol are the most useful. Acid solvents cannot be used.

### RESINS AND OTHER COMPONENTS

Among the most suitable resins are polystyrene, methyl methacrylate, and butyl methacrylate. "Acryloid" B70 is excellent, and polystyrene absorbs the least moisture. Methyl methacrylate has the highest ultraviolet transmission. Other materials which could be used are cumarone, cyclohexanone, dammar, and copal.

A good suspending medium is aluminum stearate, and an excellent stabilizer if needed is calcium borate (37), or diglyco monostearate. Dibutyl phthalate and tricresyl phosphate can be used as plasticizers, although they are not ideal. It has been stated recently that an overcoat is harmful because it does not allow the sulfurous vapors to escape. This depends entirely on the kind of sulfide and the kind of vehicle. One to 10 pounds of pigment are used in a gallon, depending on the type of sulfide. An increase of 25 to 50 per cent in phosphorescent intensity is obtainable (a tip from the firefly) by a reflector coating, to be applied first on opaque surfaces and last on transparent surfaces to be viewed from the opposite side. The white primer is made with type LO (low oil absorption pigment) antimony-free titanium dioxide as the pigment. The formula here given is representative of most formulations of this type in that it leaves much to be desired in flowing and spraying qualities. For work in some fields it would not stand up under the scrutiny of the practical paint chemist.

It is so stable and impervious, however, that it can be used outdoors with strontium sulfide. Not the slightest difference has been observed in the brightness or length of afterglow after 48 hours' immersion in cold water at 23.9° C., and it is the only one which has withstood the test of time in connection with strontium sulfide. Although the coating is porous, the polystyrene acts like an inert membrane. After immersion of 300 hours in cold water it absorbed no more than 0.05 per cent moisture. It is best applied with a brush or a paper coating machine.

STOCK SOLUTION

Polystyrene, XMS—10,023 or equivalent . . . . .	61.7 lb.
Toluol . . . . .	8 gal.
Xylol . . . . .	8 gal.
Butyl acetate . . . . .	8 gal.
Dibutyl phthalate . . . . .	2 gal.

WHITE PRIMER

Titanium dioxide Ti-Pure LO or equivalent . . .	57.5 lb.
Stock solution . . . . .	30 gal.
Naphtha—250 W Hi-Flash . . . . .	18 gal.

VEHICLE FOR SrS

Stock solution . . . . .	500 cc.
Xylol . . . . .	250 cc.
10% Aluminum stearate in toluol . . . . .	37.5 cc.
Calcium borate . . . . .	17 grams
Luminous SrS, 150 mesh . . . . .	340 grams

Hot-water extracts, made of the applied luminous coating and injected into mice and rabbits under controlled conditions, were reported as completely non-toxic. Skin irritation tests were made, and it was determined that ill effects would be encountered only by persons allergic to these specific materials, which was not considered unusual.

*Caution!* The above statements will not hold if thallium is used as an activator.

It can readily be seen why many desirable ingredients of a good surface coating must be omitted in favor of those which will permit realization to the full of the electrophysical properties of this product.

LIGHT MEASUREMENT

The decay of intensity with time is the all-important measurement. Strontium sulfide, because it has emerged as the most useful of the

long afterglow class, especially in beleaguered London (18), will again be used as the example. The photometry of these materials is difficult because the intensity happens to fall in the range in which the human eye undergoes its greatest change of sensitivity to both color and intensity. The afterglow of good commercial strontium sulfide can be seen for thirty hours or more, and it has been stated by various government authorities to be useful during this period if used in coatings of large area. The eye is quite unable to note any difference in color between two samples of the same low intensity, but the difference in color will be observed as a difference in intensity. Even if the color and intensity are the same, the one upon which the eyes are focused is less bright than another sample placed along side of it. This is important because in practice one of the samples is replaced by a standard source of light calibrated in color and intensity or in variations of intensity.

Measurements in this range, although accomplished in a few of the larger laboratories, are difficult, costly, and in a generally unsettled state. Also, they are relatively unimportant at present. Measurements in the earlier stages can be made with an accuracy of 1 per cent down to about 1 microlambert, which means the first 60 or 70 minutes of the decay period.

#### DESIGN OF VISUAL PHOTOMETERS

Since the eye is inherently incapable of measuring anything, visual photometers are comparison devices. It is a measurer of sensations, and in unskilled hands it is sometimes a psychological instrument. It is gradually being replaced by physical photometers in which no more is expected of the eye than to read a meter. There are very good reasons, however, for using a correctly designed visual instrument for measuring at least the early part of the decay curve of luminous materials. First, there is no input power during decay with which to control intensity; second, the brightness of afterglow does not vary with intensity of excitation after the threshold is reached; and, third, the decay cannot be held at any given intensity.

A seasoned incandescent lamp will, after calibration, emit an intensity with current which can be predicted, and the measurement can be carried out at any desired value by the use of screens, diaphragms, and sector wheels. The measurement can be carried out at a light value which corresponds to either complete photopic or complete scot-

topic vision. But no machine has been made which varies its input sensitivity to color with decreasing intensity as the human eye does, and, since fluorescence sources will be looked at with human eyes, they should be evaluated by human eyes.

A comparison source can be made by mounting a flashlight lamp in a reflector behind a diffusing screen of flashed opal glass. A 3-volt lamp operated at 2 volts will hold its calibration for long periods. Have the lamp calibrated at the National Bureau of Standards in connection with a high-grade ammeter. The light can be varied with a rheostat, and, if the lamp is placed in a leg of a bridge circuit which measures the resistance with variations of the filament temperature, the output will be nearly proportioned to the current. This method, however, causes a change in the spectral distribution of the source. Since a reading of only the first hour's decay is proposed, it is better to use a filter between the lamp and the diffusing screen, the color of the filter to be closely matched to the phosphorescent color, preferably matched at initial intensity, and to vary the light intensity by other methods which will not change the spectral distribution. A number of methods are available, such as a variable iris, the shutter slide, or neutral wedges. The inverse square law does not hold at these low intensities. The light can be controlled by polarization, provided nicol prisms are used. Polarizing sheet is found not suitable because of the purple color it transmits near extinction. A Lummer-Brodhun cube makes the best type of comparison screen. It should be added that a flicker disk is not suitable for reducing the light because there is a shift towards red at these low intensities. A separate color filter should be used for different phosphorescent colors. Moon (21) is the authority for the statement that, at levels of scotopic vision, an instrument such as the Macbeth illuminometer (a variation of which is proposed here) "will give correct results, provided the spectral radiosity curve of the surface is of the same shape as that of the comparison lamp." For blue-green strontium sulfide the lamp-filter combination will be peaked in the region of 500-510 m $\mu$ .

Another advantage of having a color match is that the balance point will not be affected by the visual angle of observation. Both halves or parts of the field must have equal areas. The unit can be calibrated in microlamberts.

The method suggested by the British (4) for the measurement of A.R.P. phosphorescent materials does not take into consideration the effects of peripheral vision in the examination of large areas of low



intensity (their instrument is meant to be read down to 0.1 "unit of effective brightness" = 0.1 microlambert at 2,360° K.), nor is it capable of giving a decay curve. The intensity is measured by the number of minutes required to decay to a predetermined brightness level and requires a marshaling of the senses to record a match at just the right moment. This implies an average of several readings, and this, in turn, makes it imperative that the sample in question has been previously aged by a number of excitations and quenchings, because the output is subject to the previous history of the sample before stability

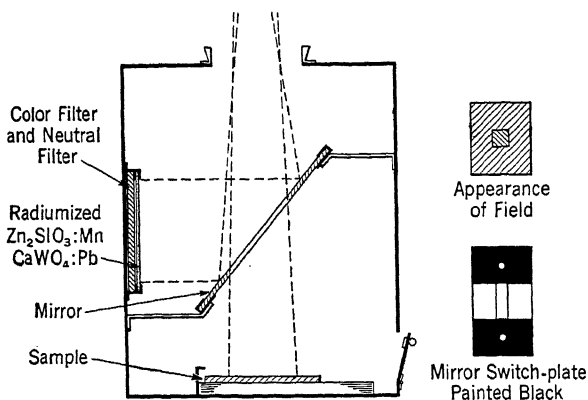


FIG. 8. Pocket Photometer.

sets in. However, the British type is recommended for use by the consumer—it is designed to measure all colors without a filter—while the suggestions for design given above are recommended for the manufacturer or experimenter. Only the decay curve, especially when used with a spectroscope of large aperture, can give the researcher the kind of information he needs by which to predict results from variation in activator, flux, temperature, and other controlling factors.

A small pocket comparator has been found very useful and a simple design which anyone can build is given in Figure 8. No electric current is necessary and the standard source of light is a disk painted with radium activated zinc orthosilicate: Mn, mixed with calcium tungstate: Pb. This material keeps its calibration much longer than zinc sulfide, because the active centers are not as easily destroyed by the alpha ray bombardment. By using these two fluorescent materials in a mixture, a color match may be obtained with the unknown, from

blue to yellow-green. Additional matching can be obtained with a gelatin filter. The mirror with a hole in it, ordinarily difficult to obtain, is a mirrored switch plate of glass, which is carried by most Woolworth stores. A simple method of operation is to add neutral filters over the comparison source until the surface brightness is reduced to exactly 1 microlambert. Then, when the sample to be measured is placed in the bottom compartment, a reading is made by noting the time required for an intensity match.

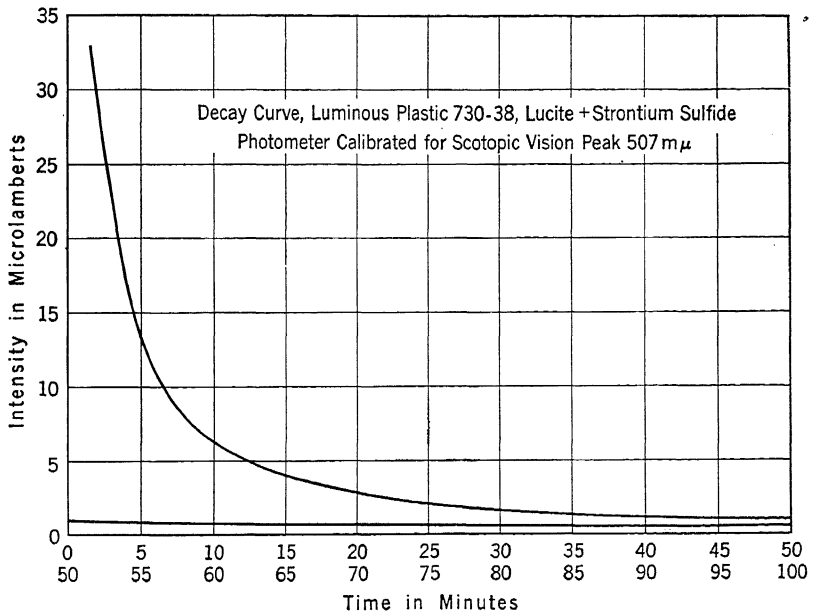


FIG. 9. Impregnated Luminous Plastic.

A recently improved type in which the phosphorescent material is laminated with flexible plastic sheeting, resulting in what may be termed a prefabricated paint film, yields a brightness of 1.8 microlamberts after 70 minutes.

#### A.R.P. USES

It is unfortunate that a war was required to awaken the public to the usefulness of luminous pigments, but it is hoped that the large-scale introduction to practice will result in postwar developments that will really utilize all the latent possibilities of phosphorescence. For the present, we can tear a page from London's book and use these materials towards preservation of life and limb in the blackout. Ac-

cording to English experience, the afterglow type should be supplemented in certain instances by fluorescent materials continuously excited by ultraviolet lamps. The uses for which the afterglow type are recommended by Levy and West, in the *London Forum* (18), and by the British Specification (4) are exit signs, direction and obstruction indicators, emergency lights of all sorts, as in subways, tanks, A.R.P. shelters, and a number of other locations of this general nature. Our own government is cognizant of these uses and specifications are now being prepared.

The author recommends that, where sufficient light for seeing by reflected light is necessary, for outdoors or uncurtained indoors, a red light is most suitable because:

1. The dark-adapted eye is not very sensitive to red light (approaching airmen).
2. Red light cannot be seen by peripheral vision (approaching airmen).
3. Red light of low intensity does not destroy dark adaptation.
4. A higher intensity could be used for seeing than would be safe with any other color. A neon glow or filament lamp could be used. For marking, or seeing the source, such as an exit light over a doorway, a blue-green phosphorescent object is best because:

(1) The dark-adapted eye is most sensitive to the blue-green, and therefore a dimmer source could be used than with any other color.

(2) Since phosphorescent sources are inherently of such low brightness, their total effectiveness is governed largely by area. Large areas of low intensity are ideal and are easily obtained with phosphorescent sources.

(3) Phosphorescent sources continue to glow after failure of power lines. A useful device would be an argon glow lamp coated with phosphorescent paint, or with a corrugated phosphorescent plastic. Printed directions and arrows are best made with regular printing inks over a large phosphorescent area. A luminous blue-green area 20 inches square can be seen at a great distance on a dark night immediately after excitation, and can be seen at 500 feet by the dark-adapted eye for 6 to 8 hours after excitation. On a moonlight night the brightness after this period of decay will be no brighter than that of a piece of white paper. It appears that the legibility of a printed notice depends more on the size of the letters than on their brightness, after a certain threshold has been

reached. At the same level of brightness and size of letters, a sign made by printing phosphorescent letters upon a black background can be read at a greater distance than a sign made with black letters upon a luminous background. But at close range, about 30 feet, the latter becomes more legible. In order to distinguish objects, the eye requires a brightness contrast of 2 per cent. Peripheral vision occurs at low intensities of light even though the eye is not dark-adapted.

The designations, Type A for zinc sulfide, having high initial brightness but short afterglow, and Type B for strontium sulfide, having low initial brightness but long afterglow, recommended by the British, are untenable, and not recommended by the author, because there are many other types having still longer and shorter periods of afterglow. Also, they have been recently called quality A and quality B, causing further confusion where none should exist.

Recent advances in the manufacture of strontium sulfide have so increased both the initial brightness and the afterglow that the use of zinc sulfide is advantageous only for the first sixty seconds. After this period the strontium sulfide remains much brighter. This test was made with the best obtainable American and foreign samples. Furthermore, what designation should be given to other materials such as the boric acid series which are so brilliant during their initial decay period that they can be seen in daylight? It follows that an expression of the intensity integrated with the time factors gives the most useful figure of judgment of various types.

### Invisible Signaling

Both fluorescence and phosphorescence have been used to some extent in signal work, but the full possibilities have not yet been explored. In the fluorescent method ultraviolet light is used as the invisible beam, and in the phosphorescent method infrared light is used as the invisible beam.

**Fluorescent Method.** In the first World War troop transports were enabled to keep visual contact with one another by the use of mercury vapor ultraviolet lamps and binoculars with fluorescent eyepieces (19). It was later found that the younger men were able to see the ultraviolet lights with the unaided eye. Dr. William Beebe has reported the fluorescence of a sample nine-tenths of a mile from an ultraviolet source. It appears that full advantage was not taken

in the above instances of the characteristics of the human eye, or of the fluorescent material, and the author proposes a method of utilizing these factors which might result in improved operation. The filters which permit the greatest ultraviolet transmission also transmit the highest percentage of visible light. The percentage of visible light could be greatly reduced by introducing an electronic "chopper" or oscillator in the lamp circuit, or, preferably, by using a sector disk operated by a motor. The intermittent ultraviolet beam would be received on a distant phosphorescent screen which has just enough phosphorescence to give a continuous light between flashes. A rate of decay of one- or two-tenths of a second, for example, is easily obtainable in a number of suitable materials.

**Phosphorescent Method.** Elaborate methods have been worked out in Europe for signaling by means of an infrared beam focused upon a phosphorescent screen in the dormant or potential state. The principle of operation is: A phosphorescent screen is continuously or intermittently irradiated by an ultraviolet source; the screen rests on a massive block of copper, the lower end of which is in contact with liquid air, which quenches the phosphorescence. When the infrared beam is focused on this screen by a lens, phosphorescence occurs in proportion to the intensity, the detail in the image depending upon the smoothness of the screen. The mechanism of infrared acceleration has been discussed in a previous section.

Many variations of this are possible. A negative image may be converted to a positive by quenching with red light, and an image may be stored at ordinary temperatures and released later by heat. The author has found that the contrast is greater when the image is stored by reduction of temperature, than by mere infrared acceleration of a bright screen decaying normally. This was demonstrated at the New York Printing Ink Production Club, March 26, 1942 (35, 36).

Whether the ultraviolet or the infrared method is superior in a light fog remains to be tested. Probably neither method would survive a dense fog. Ultraviolet light is scattered by fog, and infrared is absorbed by it. Claims of earlier workers that dense fog is more easily penetrated by infrared than by visible light are groundless (13). The wavelengths used for infrared acceleration are longer than those used in infrared photography, and range from 12,000 Å to 20,000 Å. The infrared has been photographed to 20,000 Å by focusing the infrared spectrum upon an excited phosphorescent screen.

A study of the characteristics of strontium sulfide luminous paint has been made and is offered in the hope that it might be of some

guidance to those charged with the responsibility of setting up standards and specifications for luminous paints in general.

**Excitation.** Strontium sulfide is excited by two main bands: one in the ultraviolet, at about  $320\text{ m}\mu$ , and one in the visible range at about  $436\text{ m}\mu$ . The material can be excited by daylight, or by a blue foto-flood lamp at a distance of 18 inches.

**Emission.** The color is blue-green. The spectral range is between 480 and  $520\text{ m}\mu$ . The peak is at  $500\text{ m}\mu$ . The wavelength at which the human eye is most sensitive for scotopic vision is about 507. Therefore, the color is close to the maximum sensitivity of the dark-adapted eye.

**Quenching.** The afterglow is quenched by light of longer wavelength than the emitted light, and especially by red light.

**Acceleration.** The afterglow is accelerated by infrared light of sufficient intensity to raise the temperature appreciably.

**Afterglow.** The afterglow can be seen by the dark-adapted eye for 24 hours after excitation, at a temperature of  $68^{\circ}\text{F}$ . If cooler, the afterglow will be longer but dimmer. If warmer, the afterglow will be brighter but shorter.

**Coating.** The most suitable coating thickness is about 0.011 inch.

**Stability.** The painted surface on glass, and without overcoat, will withstand a 24-hour immersion in cold water without noticeable decrease in luminosity.

**Overcoat.** The overcoat of polystyrene will withstand immersion in cold water for 24 hours with 0.00 water absorption, and after 318 hours will absorb no more than 0.05 per cent.

**Primer.** The white primer is a mixture of titanium dioxide and zinc oxide in polystyrene. The titanium dioxide must be free from antimony.

**Covering Power.** The covering power of both the primer and the luminous paint is one ounce per square foot for two coats of the proper thickness; 150 square feet per gallon. Weight—9.5 pounds per gallon.

**Viscosity.** The viscosity, measured by a stormer viscosimeter at a temperature of  $24.5^{\circ}\text{C}$ . for 100 revolutions, is 3 minutes and 25 seconds for the paint, and 6 minutes and 19 seconds for the clear overcoat.

**Containers.** The material is packed and shipped in brown glass bottles in sizes no larger than one gallon and no smaller than one ounce. The Bakelite caps of these bottles are lined with aluminum foil. The physical analysis appears on the label of each bottle.

**Settling.** The paint contains a suspended medium which prevents the formation of a hard cake when settling occurs. The settling is always soft enough to be stirred with a glass rod into a uniform paint in a few minutes.

**pH.** The pH of the luminous paint is above 7 and the pH of the primer and overcoat is 7.

Certain factors, such as the particle size and the pounds per gallon, are not important to the buyer, because the same quality of paint can be made in different ways, and these two factors can be misleading. For example, if one manufacturer uses 2 pounds of pigment per gallon of vehicle, another manufacturer might obtain undue advantage by using 6 pounds of pigment per gallon even though only 1 of 6 pounds was a luminous pigment. Since the brightness and length of afterglow are, among other things, a function of particle size, some test of brushing ability would be more advisable than a statement of the particular size. The material should not come in contact with metals other than aluminum and should be stirred with a glass rod. The length of afterglow has no meaning unless the temperature is given. The brightness of the afterglow curve in microlamberts should also contain a statement of the relative visibility, that is, whether the curve refers to photopic or scotopic vision.

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## CHAPTER 22B

### LUMINESCENT COATINGS\*

REPORT OF SUBCOMMITTEE 43 OF THE NEW YORK PAINT AND VARNISH  
PRODUCTION CLUB—PROJECT 6

#### PURPOSE

The purpose of this report is to describe luminescent paints and coatings from the standpoint of their known properties and uses at the present time, and to indicate their practical value and limitations. It is designed particularly for those persons interested in the manufacture and use of luminescent coatings. Photoluminescent coatings only are considered, and those containing radioactive materials are not included.

#### DEFINITION OF TERMS

##### Luminescent Coatings (excluding Radioactive Materials)

Luminescent coatings are coatings which have the property of converting radiant energy of short wavelength (such as black light) to visible light. They may be further subdivided into fluorescent and phosphorescent coatings.

**Fluorescent Coatings.** Fluorescent coatings are those luminescent coatings which emit useful light only during activation by black light. Such coatings may have some afterglow, but it is not long enough to be considered of practical value.

**Phosphorescent Coatings.** Phosphorescent coatings are those luminescent coatings which glow when activated by short wave visible as well as black light, and continue to glow for appreciable intervals after the exciting light source is extinguished. In order to be considered phosphorescent, the afterglow must have a useful length of a few minutes to twelve hours or more.

\* We wish to thank the *Official Digest*, official publication of the Federation of Paint and Varnish Production Club, for permission to reprint this "Luminescent Coating Report," which appeared in the February issue, 1942.

Phosphorescent coatings are divided into two classes.

*Phosphorescent Coatings—Type A.* Type A phosphorescent coatings have a high brightness during the first few minutes after excitation ceases, and the useful afterglow is relatively short, usually two hours or less.

*Phosphorescent Coatings—Type B.* Type B phosphorescent coatings have a relatively low brightness shortly after excitation ceases, and the useful afterglow is relatively long, usually two to twelve hours.

### **Black Light**

Black light is the popular designation for the invisible near ultraviolet radiant energy most commonly used to produce fluorescent and phosphorescent effects. Its spectral range is approximately 3,200 to 4,200 Å.

## **FLUORESCENT COATINGS**

### **Inorganic Pigments**

Whereas a number of inorganic materials are fluorescent and useful as pigments, those of principal practical value are zinc sulfide or combined zinc and cadmium sulfides. Such pigments compare with lithopone or other zinc sulfide pigments in their paint-making properties and characteristics. They are relatively fine in particle size, may be incorporated in binders (vehicles) on standard paint milling equipment, and yield normal paints. A range of fluorescent colors extending from green through yellow, orange, and deep red is available. The colors of the pigments in visible light do not correspond to their fluorescent color. In some cases, organic dyes or other tinting materials are added to modify either the color in visible light or the fluorescent color. The addition of such tinting agents may somewhat decrease the fluorescent intensity. Inerts or extenders of the quality used in paints may also be added to modify the physical characteristics of the liquid paint but only at some sacrifice in fluorescent intensity. Under some conditions of exterior exposure in certain vehicles, there is a tendency to darken with accompanying loss of fluorescence. From the standpoint of toxicity, these pigments are no more hazardous than other regularly used paint pigments.

### **Synthetic Organic Dyes and Pigments**

The most important organic compounds that fluoresce are dyes. Many dyes give a brilliance under black light that is not equaled by any known natural minerals and by very few, if any, luminescent pig-

ments. Dyes in powder form rarely fluoresce as brilliantly as when applied to textile fibers. Luminescent coatings are prepared by dispersing spirit- or oil-soluble dyes in binders. The most important groups of spirit-soluble dyes are:

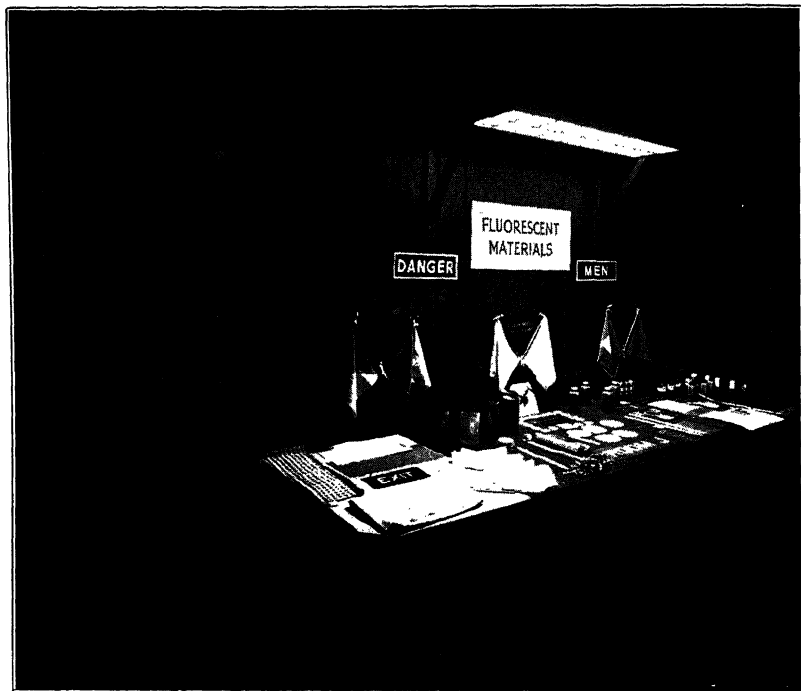
Rhodamine

Eosine

Auramine

Thioflavine

Phosphine



*Courtesy of National Paint, Varnish and Lacquer Association*

Fluorescent Objects Photographed in Completely Dark Room by Their Own Light. Exposure up to 15 Minutes.

The oil-soluble dyes used are limited chiefly to oleates or stearates of fluorescent basic dyes. For greater light fastness but with some sacrifice in fluorescent brilliance, organic pigments are used. They are represented by:

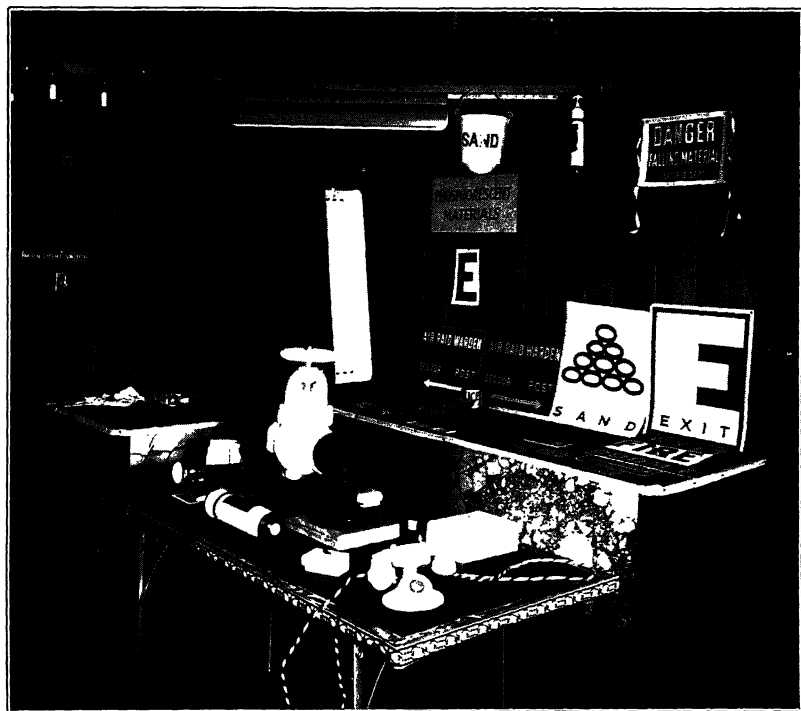
Sodium Red Lake C Toner

Rhodamine Tungstate Lake

Auramine Tungstate Lake

Metallo-organic compounds, as the zinc salt of 8-hydroxyquinoline, have been used in England. Experiments have shown that molybdate lakes also fluoresce, and these may assume practical importance in the future. Other organic materials show fluorescence, but their practical importance remains to be demonstrated.

Although a wide range of shades can be obtained with fluorescent dyes on textiles, at present in formulating coatings the choice of these



*Courtesy of National Paint, Varnish and Lacquer Association*

Phosphorescent Materials Photographed in Completely Dark Room by Their Own Light. Exposure up to 15 Minutes. (Articles on Table in Foreground Have Baked Phosphorescent Finishes.)

dyes is limited, owing to their lack of solubility in non-aqueous media. Chemical modifications to make them spirit- or oil-soluble may result in loss of fluorescent properties.

These organic fluorescent dyes have very little resistance to sunlight, and consequently their use outdoors must of necessity be limited. Exposure to direct sunlight results in rapid loss of fluorescent charac-

teristics. The metallo-organic compounds are reported to have somewhat improved weather resistance.

None of the organic compounds under discussion show useful phosphorescent properties. Where phosphorescence is desired, inorganic pigments must be used.

Fluorescent dyes are generally considered to have a low degree of toxicity, and have been used in the past in coating compositions without any difficulty in this respect.

### Characteristics and Limitations

Fluorescent coatings have been employed in the theatrical field for many years to obtain unusual lighting, decorating, and staging effects. Their potential value for novelties and in the advertising field is recognized. They are being used for direction guides during blackouts on instrument dials, maps, and charts where black light activation is practical. The range of colors is wide, and the fluorescent brilliance varies with the power of the black light. The usefulness of these finishes is limited by the availability, portability, and cost of the black light units. Fluorescent coatings will pick up to nearly full intensity of luminescence with a flash of activating "black light." In general the faster this pick up, the shorter the afterglow when the exciting light is extinguished.

From the standpoint of durability, fluorescent coatings are quite permanent when used *indoors*, without exposure to direct sunlight. When used *outdoors*, or under conditions of exposure to direct sunlight, coatings made with organic dyes are subject to the rapid loss of color and fluorescent properties. Experimental results have indicated that coatings made with inorganic pigments, properly formulated, may retain more than fifty per cent of their fluorescent brilliance after a year or more of exterior exposure.

A lowering of temperature will tend to increase whatever afterglow the fluorescent coating may have.

### PHOSPHORESCENT COATINGS

The Type A phosphorescent pigments in most common use are zinc sulfide or zinc and cadmium sulfides, and the Type B are calcium sulfide, strontium sulfide, or combinations of the two. All phosphorescent pigments are relatively coarse in particle size since their phosphorescence depends upon a coarse, crystalline structure. They cannot be ground on a tightly set roller mill or a stone mill without a serious loss

in their phosphorescent efficiency. They are best incorporated in vehicles by stirring, mixing, or on a very loosely set roller mill. The range of phosphorescent colors is relatively small, Type A pigments usually having a green, yellow, or orange phosphorescence, and Type B a violet-blue or bluish green phosphorescence. The color of the materials in visible light is a dull white, with a grayish or yellowish tinge. Because of their extreme coarseness, phosphorescent coatings do not have very high hiding or whitening power, and occasionally white pigments such as titanium oxide, lithopone, or zinc sulfide are blended with them to supplement these characteristics. At times tinting pigments or dyes are added to modify either their color in visible light or their phosphorescent color. Inert extenders may be added to improve the physical properties of the liquid paint. Such additions should be avoided if at all possible, since they tend to decrease phosphorescence. Because of their extreme coarseness, all phosphorescent pigments have poor gloss characteristics and a marked tendency toward settling.

Type A pigments behave in paint vehicles in a manner similar to lithopone and zinc sulfide. Type B pigments are quite reactive and are also extremely sensitive to moisture, which destroys phosphorescence. They must be stored in moistureproof containers and must be used in coating compositions in such a way as to be protected from moisture. Under some conditions of exterior exposure in certain vehicles, there is a tendency for Type A pigments to darken with accompanying loss of phosphorescence. From the standpoint of toxicity, these phosphorescent pigments are no more hazardous than other pigments regularly used in paints. It must be emphasized that this report does not apply to radioactive materials.

### Characteristics and Limitations

Phosphorescent coatings also have found application in the theatre for producing unusual staging and costuming effects. Their use in the novelty field has been more extensive than that of the fluorescent finishes, and their possibilities for general interior decoration are becoming more widely recognized. They may find further application for *interior* use as markers for exits, guide lines, obstructions, etc., in public buildings, industrial plants, transportation systems, air raid shelters, ships, and homes during power failure or blackout. For *exterior* applications, the potential usefulness of phosphorescent coatings is somewhat more limited because of the low visibility, as explained later. However, they may find some use on markers, directional signs, large obstructions, and for treating the clothing of pedestrians. The use of

phosphorescent coatings in certain phases of camouflage work has been suggested. It must be emphasized that the larger the area painted, the greater the potential visibility and usefulness of these finishes.

It is difficult to make phosphorescent coatings comparable in appearance to ordinary paints because of the coarseness of the pigments and the lack of color range both in phosphorescent and in visible light. Paints made with these pigments have poor flow; also rapid and hard settling. The Type B pigments must be protected from moisture by a clear film of vehicle, or a layer of glass or other transparent covering.

Phosphorescent coatings are used because of their afterglow. However, the intensity of this afterglow is quite low and its duration is limited, so that the coatings are not always so useful as is desired. The intensity of the afterglow, immediately after activation ceases, is between 1 and 10 per cent of the fluorescent intensity during activation. Phosphorescent coatings are therefore useful only under conditions of extreme darkness and can generally be detected only when the eye has become adapted to the darkness.

When used *indoors* where conditions of complete darkness exist, Type A materials can be seen by the dark-adapted eye for 4 to 8 hours, have a moderate intensity for about 2 hours, and can be readily perceived for 1 hour. Type B materials can be seen for about 24 hours, have a moderate intensity for about 10 hours, and can be readily perceived for 3 or 4 hours. When used *outdoors* their value in comparison with white coatings will be dependent upon the amount of visible light available. On a clear, moonless night, the amount of light from the sky is sufficient to illuminate a white paint to a brightness equal to or greater than that of most phosphorescent coatings. Only on extremely dark nights or in narrow streets, shadowed by high buildings, do such coatings show a higher brightness than that of a good white paint.

Phosphorescent coatings generally require an appreciable time of activation to come up to full intensity. In Type A materials this time may be 10 seconds to a minute, and for Type B materials 1 to 10 minutes, depending on the intensity of the light source.

From the standpoint of durability, these finishes are quite permanent when used *indoors*. Experimental results have indicated that coatings made with Type A pigments, properly formulated, may retain more than 75 per cent of their phosphorescent brilliance after 9 months of *outdoor* exposure. Coatings made with Type B pigments are generally considered useful for not more than 6 months of exterior exposure.

A lowering of temperature will appreciably increase the length of afterglow and decrease its intensity.

### BINDERS

The principal requirements of the binders (vehicles) used to make luminescent coatings are:

1. They should be pale in color and transparent to ultraviolet and short wavelength visible light.
2. They should be practically neutral and non-reactive with the pigments and dyes. Even a low acidity may prove objectionable.
3. They should be non-yellowing on aging.
4. They should have a high degree of moisture resistance.

The binders may be either air-drying or baking types. Herewith is given a list of those which have been reported as having been successfully used.

#### Air-drying binders (vehicles):

1. Alkyds (drying oil type).
2. Cellulose nitrate and acetate.
3. Chlorinated rubber.
4. Dammar.
5. Highly polymerized drying oil cut with zinc resinate.
6. Maleic ester oleoresinous.
7. Methacrylate.
8. Polystyrene.
9. Vinyl resin.

#### Baking binders (vehicles):

1. Alkyds.
2. Melamine alkyd.
3. Urea alkyd.

For exterior use, binders with good durability characteristics should be chosen. Some alkyds and reduced phenolics may prove objectionable because of acidity.

### Driers

Many of the binders used in luminescent paints require added driers to secure the desired drying. Metallic driers should be used in as small



amounts as possible. It has been found that generally manganese is the safest drier to use; limited amounts of lead may be used with most luminescent pigments and dyes without impairing their luminescent properties. Some authorities have found cobalt to be definitely injurious. All metals may be injurious to certain luminescent pigments and dyes, and consequently it is advisable to check carefully any drier combination to determine the effect on the luminescent properties of the finished coating.

### **Solvents**

Most solvents commonly used in the paint and coating industry can be safely used in luminescent finishes. However, those solvents should be avoided that have an acid reaction or may decompose to form acids, such as some esters.

### **Packaging**

Very little is known about the influence during storage of metal containers upon the luminescent properties of luminescent paints. The safest known procedure is to use a can coated with baked finish or a glass container.

## **ACTIVATION (LIGHT SOURCES)**

Since fluorescent luminescent coatings have no appreciable lag, only black light with little or no visible light should be used as an activating agent. Suitable sources are mercury vapor, argon glow, and fluorescent and incandescent filament lamps. They are generally used with filters to absorb most of the visible light.

Because the phosphorescent coatings continue to glow after the activator (light source) has been removed, a true black light is unnecessary. Any of the previous light sources without filters can be used as activators and, in addition, they may be excited by daylight.

### **Mercury Vapor Lamps**

These light sources produce appreciable energy in the black light region and are the most powerful activators available. Because of their line spectra, the energy is more easily filtered to produce black light. The sizes available at present range from 100 watts up to 3,000 watts. Each of these requires an individual transformer for satisfactory operation. This consideration may limit their use to more or less permanent mountings and certainly to a-c circuits. Since mercury

lamps require several minutes to warm up, they cannot be switched off and on rapidly.

### Argon Glow Lamps

The commercially available argon glow lamps produce very little visible energy, but radiate an appreciable amount of invisible energy in the black light region. They may, therefore, be used with or without filters, depending on the degree of black light desired. These lamps, having low operating current characteristics and operating equally well on alternating or direct current, may be adapted to operation from batteries and can, therefore, be considered quite portable.

### Fluorescent Lamps

These lamps radiate an appreciable amount of black light and are efficient and effective activators. The 360BL lamps are made especially for the activation of *fluorescent* materials. They will, in general, be used with filters to absorb visible light. However, since these lamps give very little visible light and since they operate at relatively low wattages per unit area, it is not necessary that dark heat-resisting glass be used as filter material. Pot blue glass is quite suitable for this purpose.

For *phosphorescent* paints and coatings, the ordinary 3,500-degree white, daylight, and blue fluorescent lamps are very effective activators. The 360BL lamps may also be used if desired.

The linear characteristics of fluorescent lamps make them particularly adaptable to extended areas such as panel boards, signs, and murals.

Fluorescent lamps are basically a-c devices. They require a reactor or current-limiting device for each lamp or for each pair of lamps.

Special auxiliaries are available for the operation of fluorescent lamps on direct current. With them, however, the losses in the current limiting ballast are much greater than on alternating current.

### Filament Lamps

The amount of energy in the black light region produced by this type is small. These, such as the foto-flood lamp, with filaments operating nearer to the melting point of tungsten and consequently with a much shorter expected life, produce the greatest quantities of active radiations. Since these sources are inefficient in the production of black light, it becomes necessary to use relatively high wattage

sources. This necessitates the use of filters having high absorption in the visible portion of the spectrum as well as excellent heat-resisting characteristics. However, filament lamps operate equally well on alternating or direct current and, therefore, are used where this consideration is of prime importance.

If a low-intensity portable source of black light is required, a flash-light can be equipped with the proper filter.

### APPLICATION

It is advisable to apply a white undercoat to surfaces to be coated with luminescent paints. Such undercoats should not contain metals or pigments which would be detrimental to the properties of the luminescent coating. It is advisable to apply two coats of luminescent coating to insure perfect coverage and maximum efficiency.

Since the Type B phosphorescent pigments and the fluorescent dyes are sensitive to moisture, it is necessary to apply a clear, pale finish coat which is transparent to ultraviolet and short wavelength visible light. It has been found that if a properly selected clear finish coat is used, the efficiency of the luminous paint is not materially impaired. The clear finish also improves the washability of coating. The undercoat, luminescent paint, and the clear finish can be applied by any of the well-known methods of application such as brush, spray, roller coating, and dip.

### METHODS OF TEST

The methods of test and evaluation of luminescent pigments are in need of standardization. The following specifications and tentative specifications describe test methods:

BS/ARP-18—British Standard Specification for Fluorescent and Phosphorescent Paint (excluding Radioactive Materials) for A.R.P. purposes, July, 1940.

BS/ARP-32—British Standard Specification for Illuminated and Nonilluminated A.R.P. Signs, British Standards, Institute, May, 1940.

Lacquers, Fluorescent—Instrument Marking. Air Corps Specification 14,102, June 26, 1940.

Markers, Fluorescent—Instrument Identification and Range. Air Corps Specification 17,012, July 19, 1940.

Paint, Luminous Nonreactive—Rock Island Arsenal. Tentative Specifications RIXS-122—Rev. 1, January 24, 1941.

**NEW YORK PAINT AND VARNISH PRODUCTION CLUB  
SUBCOMMITTEE No. 43**

**LUMINESCENT COATINGS**

**COMMITTEE ORGANIZATION**

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Frederick C. Schmutz	New Jersey Zinc Co.
Roy A. Shive	Calco Chemical Division
George F. A. Stutz	New Jersey Zinc Co.
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*Editor's note:* There may be some difference of opinion existing in some instances between this chapter and Chapter 22A. The editor has permitted this purposely because he believes that different students of the same subject may view similar results differently.



## PAINT MANUFACTURING PROCEDURE



## CHAPTER 23

# PAINT MIXING AND GRINDING OR DISPERSION EQUIPMENT

CARL M. FREY

### Introduction

In the manufacture of pigmented paint products many different types of equipment are required to disperse the pigment particles in the vehicle thoroughly. In order to obtain the degree of dispersion desired, the pigment must first be mixed with some of the vehicle to produce a semi-paste. This mixing action partially wets the dry pigment but at the same time forms agglomerate masses of semi-wetted pigment. These agglomerates consist of lumps, the outer layer of which is made up of wetted particles, the next layer of semi-wetted particles, and the inner section of dry particles. Prolonged mixing will eventually break down these agglomerates but, since time is costly, some other means must be utilized to speed up the dispersion. This is accomplished by means of grinding equipment in which the agglomerates are broken up and the pigment dispersed in the vehicle as the semi-paste mass is forced to pass between the grinding surfaces. The degree of dispersion is controlled by the amount of clearance between the grinding surfaces; and the finer the grind given to a material the better will be the dispersion and the smoother the film of the finished product.

The degree of dispersion required is dependent upon the type of material being manufactured and how it is to be used. Some products if ground too fine will not be materially benefited, and at the same time the cost of manufacture will be so increased that they will not be competitively salable.

Some machines combine the mixing and grinding operation in one; others require the preparation of a semi-paste separately, which is then fed to the grinding machine. Some types of equipment are water-cooled; others are not. In the grinding operation heat is generated, and in certain vehicles this is detrimental to the product being proc-



essed as the vehicle thickens and polymerizes and so becomes unusable. The water cooling of the grinding surfaces prevents this heat reaction. Furthermore, heat will sometimes cause a change in color of the pigment being used.

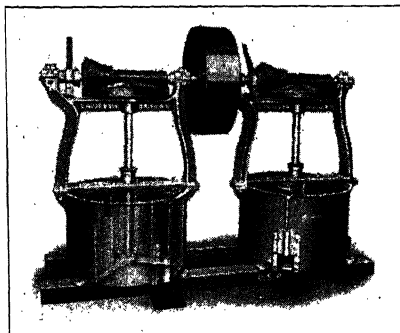


FIG. 1. A Typical Lead Mixer.

In this mixer the revolving stirrer consists of three wings from which project upward several arms on each wing. Mounted across the top of the vat is a stationary cross bar from which extend downward several arms on each side of the stirrer shaft. When the bottom stirrer revolves, its upright arms pass between the vertical stationary arms. The wings of the revolving stirrer sweep over the bottom of the vat and force the material between the upright blades, mixing it thoroughly. When the mixing operation is finished the resulting mixture can be discharged through the gate at the bottom into a suitable collecting vessel or directly to a grinding machine.

These mixers range in capacities from 45 gallons up to 350 gallons, and are generally used for making heavy pastes.

**Pony Mixer.** Figure 2 shows the construction of a typical pony mixer. In this mixer the tub is caused to revolve on a platform. Extending down into the tub is a series of blades which also revolve, but in an opposite direction. This double action imparts a thorough mixing to the entire contents of the tub.

### Paste-Mixing Equipment

This equipment generally consists of a vat in which some type of stirrer is caused to revolve and thereby mix the dry pigment with the vehicle. Some of the more commonly used types of mixers will be briefly discussed and illustrated.

**Lead Mixer.** Figure 1 shows the construction of a typical

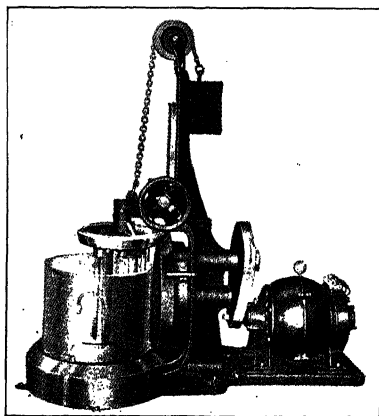


FIG. 2. A Typical Pony Mixer.

These mixers range in capacities from 15 gallons up to 125 gallons and are generally used for making enamel pastes and soft color pastes.

**Abbé-Lenart Mixer.** Figure 3 illustrates a mixer of this type. In this mixer a disk equipped with curved radial ribs rotates horizontally

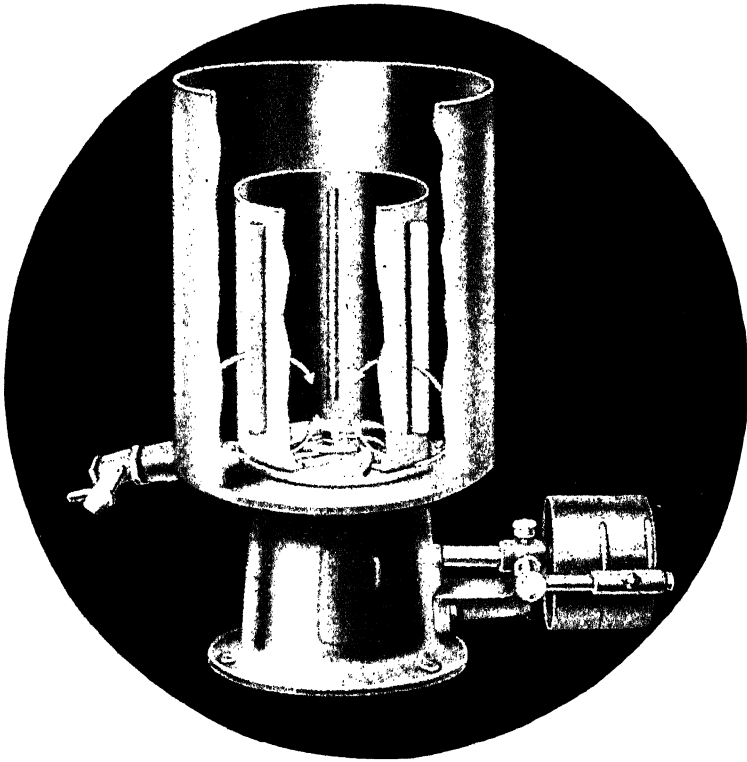


FIG. 3. An Abbé-Lenart Mixer.

below a stationary cylinder equipped with vertical slots, with outwardly projecting baffles at each slot.

The mixing and dispersing action is caused by the centrifugal force developed by the high-speed rotation of the horizontal mixing disk. Material is thus forced through the narrow opening between the mixing disk and the stationary cylinder into the space between the inner wall of the tank and the outer surface of the stationary cylinder. Thus a spiral circulating movement is set up which causes the material to flow against the baffles. Some of the material is forced

through the slots back into the curved mixing disk, while the remainder of the material flows back over the rim of the stationary cylinder. By repeated passings through this cycle the desired mixing is accomplished. The mixed paste can then be drawn off through the discharge spout.

These mixers range in capacities from 11 gallons up to 330 gallons and can be used for making soft semi-pastes. These mixers can also

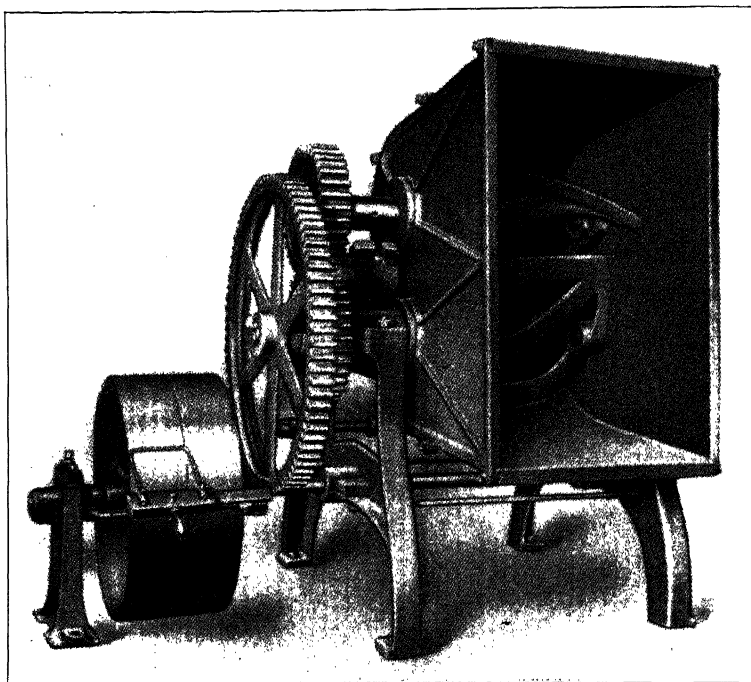


FIG. 4. A Dough Mixer.

be used for making certain types of paints where fine grinding is not required.

**Dough Mixer.** Figure 4 illustrates a mixer of this type. In this mixer the two spiral blades revolve so that each passes through the path of the other, thereby thoroughly cutting up and mixing the paste mass. After the batch has been completely mixed the tank can be tilted and the material discharged while the machine is still running.

These machines range in capacities from 50 gallons up to 100 gallons and are mainly used for heavy pastes.

### Grinding Equipment

**Stone Mills.** Figures 5 and 6 illustrate typical single stone and tandem stone mills. The flat stones are set in finished casings, which are adjusted so that the hinge ring compensates for wear of the stone surfaces. The top stone is stationary and has a circular opening called the "eye," through which the paste material is fed into the mill. The bottom or "runner" stone revolves and carries the material through the mill. By means of a lever arrangement the faces of the stones

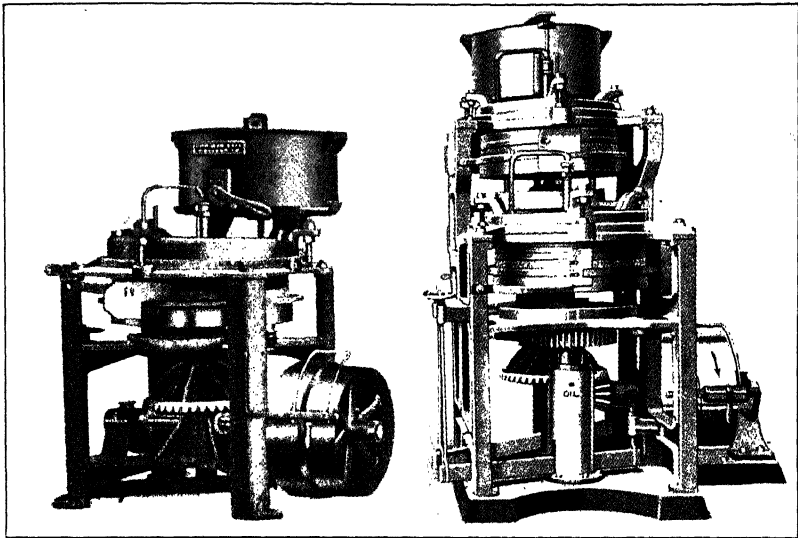


FIG. 5. A Typical Single-Stone Mill. FIG. 6. A Typical Tandem Stone Mill.

can be brought together or separated. The distance between the stone faces controls the production output of the mill and the degree of fineness of grind. The stone casings are designed so that they can be water-cooled if necessary. A feeding hopper is attached to the mill so that its discharge outlet is directly over the "eye" of the top stone. In this hopper is a sweep which revolves when the mill is running, thereby keeping the paste mixed and also forcing it out of the discharge port. The amount of paste discharged is controlled by the degree the discharge port is opened. The speed of the mill is regulated so that the paste does not pass through too fast and thereby prevent the stones from grinding the material properly. Sometimes an iron mill feeder is used in place of a feeder hopper. The object of this iron mill feeder

is to give a preliminary grind to the paste and also to insure a uniform feed to the mill.

The surfaces of the stones are usually dressed as shown in Fig. 7. In Fig. 8 are illustrated the various characteristics required in dressing a stone together with a chart giving the respective dimensions for the various sizes of mill stones.

The "eye" of the bottom stone is completely filled and encloses the end of the driving shaft, which causes it to revolve and is built up in the shape of a small mound, as shown in Fig. 7. When the stones are

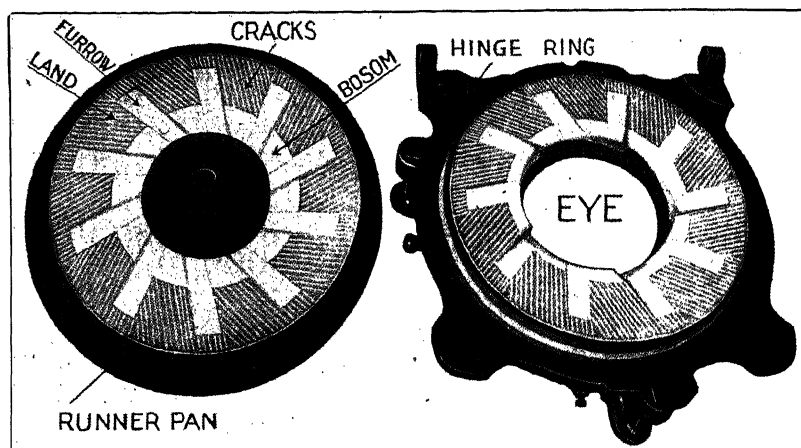
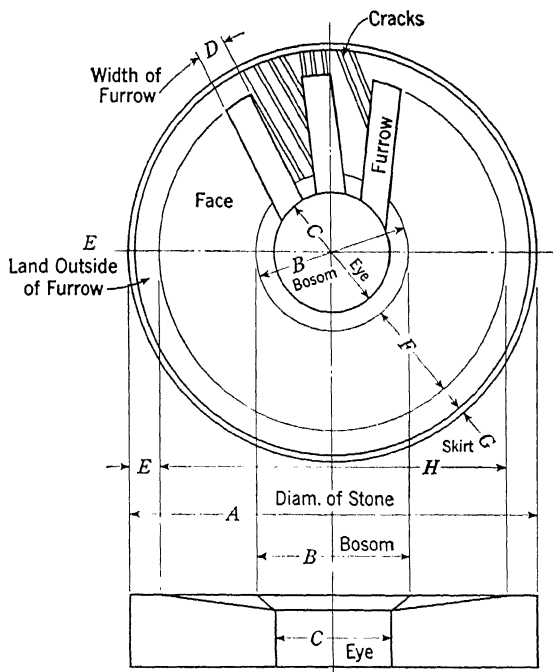


FIG. 7. Dressing of Stones.

in place the cracks of the top stone are diagonally across those of the bottom stone and form a diamond-shaped gridwork. The maximum amount of paste which the stone will handle is governed by the depth of the "bosom," which in turn is controlled by the diameter of the stone. It is further possible to control the rate of production and degree of dispersion by increasing or decreasing the distance between the grinding surfaces and also by increasing or decreasing the amount of paste being fed into the mill.

The paste, on being fed into the mill, is deposited on the sides of the mound of the runner stone and from there works down into the bosom and furrows. Centrifugal action carries the paste out through the furrows to the cracks. In the meantime, a spiral motion has been imparted to the paste, and as it passes into the cracks it is forced out over the edges of the cracks onto the face of the stone. This gives a cutting action which tends to break up agglomerates and help dis-

perse the pigment. As the material slides across the face of the stone a smearing action results which further breaks up pigment agglomerates. These two actions are repeated many times as the material is



Stone Dress Chart for M.No.9 Stone Mills																
A	B		C		No of Furrows	D	E	F	G	H	Cracks			Depths		
	Top	Runner	Top	Runner							No. Inch	Width	Depth	Furrows	Bosom	Total
16"		10"	8"	6½"	8	1½"	1"	2"		14"	5	1/16"	1/16"	¼"		¾"
20"		12"	10"	8½"	9		1¼"	2¼"		18"					⅛"	½"
26"		16"	13"	10"	10	2"	1½"	3½"		23"	4			⅜"	¼"	⅝"
30"		18"		12		1¾"	4¼"	½"	26½"	3						

FIG. 8.

forced out over the edge of one crack onto the face of the stone and into the next crack, until the material has traveled over the face of the stone to the outer edge or "skirt," where a final smearing action is imparted. It is then taken off the edge of the runner stone by means of

a perpendicular scraper blade placed at a tangent to the outer circumference of the stone, as can be seen in Figs. 5 and 6.

Sometimes, in order to increase the production of a mill, the stone is dressed without a skirt and the cracks carried out to the edge of the stone.

The size of stones used ranges from 16 inches to 36 inches in diameter.

When double grinding is desired, tandem mills are used. The time necessary for this double grinding is approximately no greater than that consumed in a single grinding because the paste is discharged from the first pair of stones and fed directly to the second pair of stones. The power required to drive a tandem mill is about one and two-thirds of the amount required to drive a single mill of the same size.

Stone mills are not very flexible and are devoted generally to one type of color only. This is due to the fact that the stones are partially porous and retain color particles in the small fissures as well as the cracks and furrows, and these are not readily removed without prolonged and extensive cleaning.

Stone mills are generally run in gangs of four to six mills. They require the constant attention of an operator to regulate the setting of the mills and to control and maintain a uniform feed of paste to the mills.

When the dressing on the face of a stone is worn down so that it no longer operates efficiently, the frames holding the stones can be readily removed from the mill and the stones redressed. Generally a dressing will last from four to six months, depending upon the abrasiveness of the material being processed. The average pair of stones can be redressed in one to two days. To insure good grinding it is therefore necessary to check the dressing periodically and, as soon as signs of wear appear, to have the stone redressed. These signs of wear are easily recognized by loss in depth of the bosom, furrows, and cracks, and also by the tendency of the cracks and the land between them to become one smooth surface.

The 16-, 20-, and 26-inch mills are extensively used for grinding tinting colors, colored enamels, and a general line of paints. The 26-, 30-, and 36-inch mills are used for general house paints, flat wall paints, stipple paints, gloss whites, and semi-paste paints.

**Roller Mills.** The roller mills as used in the paint industry are generally equipped with hardened steel rolls which are hollow in order that the roll may be internally water-cooled. These mills are equipped

with either three, four, or five rolls, which are generally mounted in the machine as illustrated in Fig. 9. Three roller mills are generally mounted in the horizontal plane. Those equipped with more than three rolls may be mounted in any of the methods illustrated in Fig. 9.

In Figs. 10 and 11 are shown typical three- and five-roller mills. The theory of grinding is the same on these mills except that the greater the number of rolls, the more points of contact and of grinding action. The rolls are mounted in the framework of the machine so

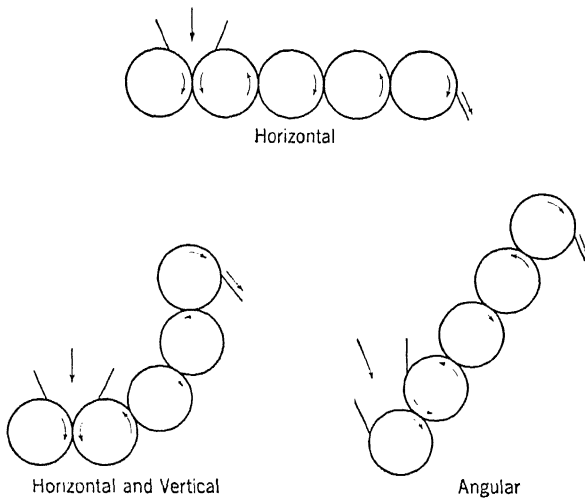


FIG. 9.

that by adjusting handwheels which operate worm gears the rolls can be moved against or away from each other. The mills are equipped with a feeding control device called regulator guide blades or hopper. This device is mounted on the feeding side of the mill over the first and second rolls as shown in Figs. 10, 11, and 12. The ends of this device are constructed so that they conform to the circumference of the rolls and fit down in between the two rolls almost to the point of contact and just barely clear the surfaces of the rolls. Thus it keeps the material from running over the edges of the rolls, and only a very small amount of paste is able to get between the guide blade and the roll surface. This small amount of paste acts as a lubricant and prevents friction and wear on the roll surface.

When the rolls are brought together a line of contact is established across the entire length of the roll. Since the rolls revolve at different rates of speed, the first roll being the slowest and each succeeding roll



faster, then a given amount of surface of one roll will slide past a greater amount of surface of the next succeeding roll. Thus a rubbing

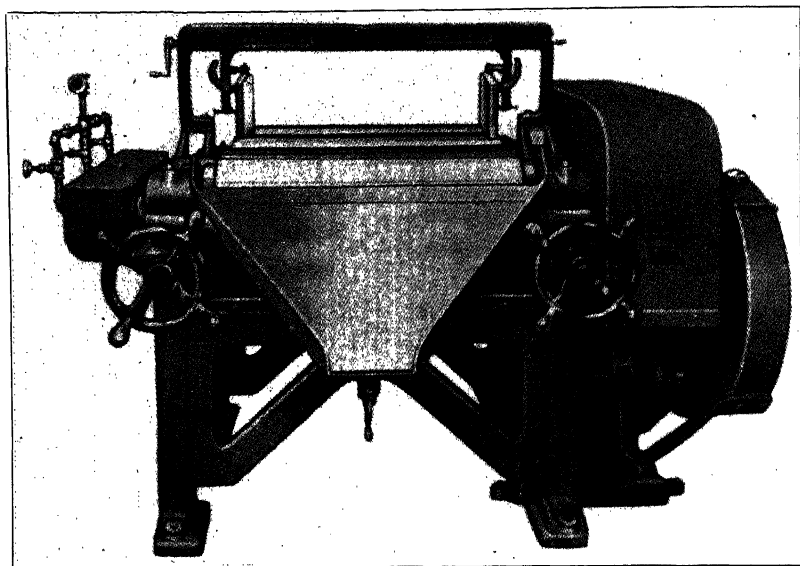


FIG. 10. Three Roller Mill, Front View.

action takes place, and the paste between any two rolls is sheared and smeared out to a thinner film on the next succeeding roll. It is

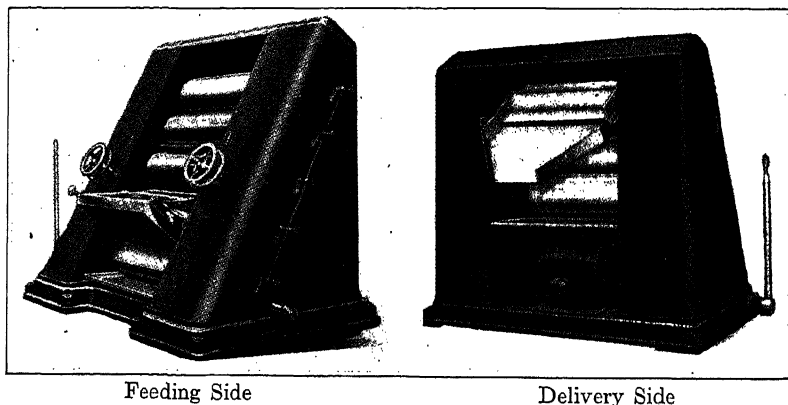


FIG. 11. Five Roller Mill.

this action which breaks up the agglomerates and further disperses the material in the vehicle.

The speed of the rolls is such that the rate of each succeeding roll is approximately twice that of the preceding.

The rotational direction of the various rolls in a five-roller mill is shown in Fig. 12. As paste is fed between the first and second rolls, a certain amount of paste is rubbed onto the surface of the second roll revolving away from the line of contact. This is then carried towards the next succeeding roll where a similar rubbing action is repeated. Thus the material travels from roll to roll until it is finally carried to the last roll. Thus a three-roller mill subjects the paste to two rubbings; a four-roller mill to three rubbings; and a five-roller mill to four rubbings.

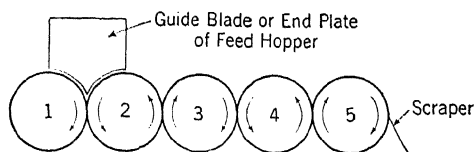


FIG. 12.

The paste delivered to the last roll is scraped off onto the apron by means of a scraper knife, running across the entire length of the roll and placed at an angle to the roll as shown in Fig. 12. By means of an adjusting device this scraper knife is brought just in contact with the roll at the proper angle to remove the ground paste.

The size of the rolls usually ranges from a diameter of 9 inches and a length of 22 inches to a diameter of 16 inches and a length of 40 inches.

The roller mills are very flexible and are quite readily cleaned. Because of the extreme hardness of the roll surface very little color is retained in the pores of the metal and therefore the rolls can be easily cleaned off. Since the rolls are very accessible, no dismantling of the machine is required to clean it.

These machines require the constant attention of an operator to adjust and feed material to the mills, but do not require quite so much attention as stone mills.

When the rolls become worn and no longer run true, it is necessary to regrind the roll surface. In order to do this the mill must be dismantled and the rolls removed. This requires considerable time, and usually a mill being redressed is out of operation one to two weeks. It is a fact, however, that roller mills with proper care and handling require very much less redressing than stone mills, and generally need be redressed but once in three or four years.

Materials containing siliceous and abrasive components are not processed usually on roller mills because of the excessive wear caused by this type of material. Roller mills are most used in the processing of enamels and other types of products where extremely fine grinding and dispersion are required.

**Bramley Mills.** This mill consists of a stationary shell, properly water-jacketed, the inside circumference of which is lined with interleaved liners. These liners are made up of steel strips and special fiber strips installed alternately in the cylinder, thereby producing a laminated surface. Inside the shell are a series of grinding blades

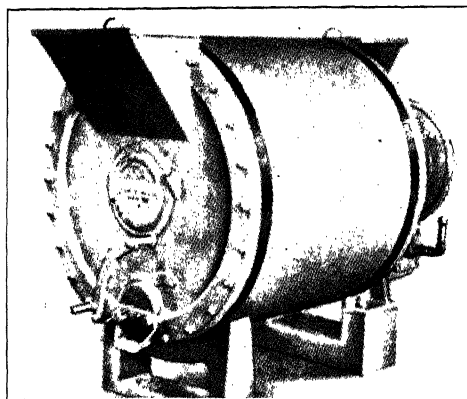


FIG. 13. Bramley Mill.

arranged as shown in Fig. 14. By means of a suitable device, pressure can be applied to the grinder blades, forcing them against the laminated surface.

The grinding vehicle is put into the machine through the loading hopper. The mill is then started and allowed to run with no pressure on the grinder blades. The dry material is then fed through the loading hopper and, after all of it has been put into the mill, it is allowed to mix for a length of time before pressure is applied to the grinder blades. When pressure has been applied to the blades which run the full length of the shell, any material between the blades and the laminated surface is subjected to an intense rubbing, wiping, and shearing action as these blades sweep over the laminated surface. This action is continued as long as is necessary to obtain the desired degree of dispersion, and the material can then be removed through the discharge valve located at the bottom of the machine as shown in Fig. 14.

In this type of machine, mixing and grinding are carried out in the same unit. It requires no attention other than starting, loading, and discharging, and the adjusting of the pressure on the grinder blades.

These machines are usually employed on thin semi-pastes, and the degree of dispersion is dependent upon the pressure applied to the grinder blades and the length of time the material is processed in the machine.

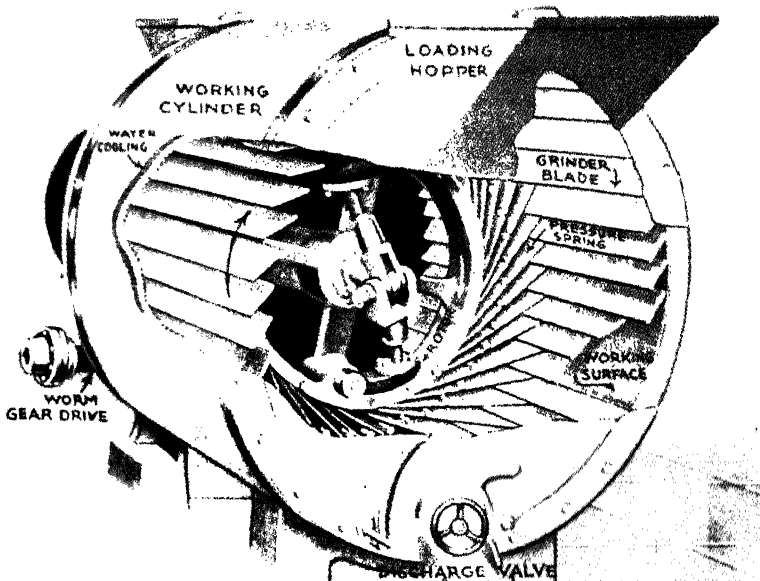


Fig. 14. Cross-Sectional View of Bramley Mill.

These machines range in capacities from 20 gallons to 158 gallons.

This type of machine is primarily a one-color machine, and is not very readily cleaned. In order to clean it thoroughly, we must charge the machine with a suitable cleaning fluid and run it for a period of time in order to dissolve and loosen up the paint. After this fluid is removed the entire head of the machine must be taken off to get at the grinder blades and the revolving mechanism to which they are attached and at the laminated surface. These parts can then be wiped thoroughly clean.

The grinding blades can be replaced rather easily when worn; but, when the shell lining is worn out, it is necessary to take the machine apart and have the shell relined, a lengthy and expensive operation.

Where a sufficient number of one size of the machines are in operation, it is customary to carry a spare shell to save on lengthy and costly shutdowns.

An outstanding feature of this type of mill is that it can be operated with very little manual attention. Likewise because it is com-

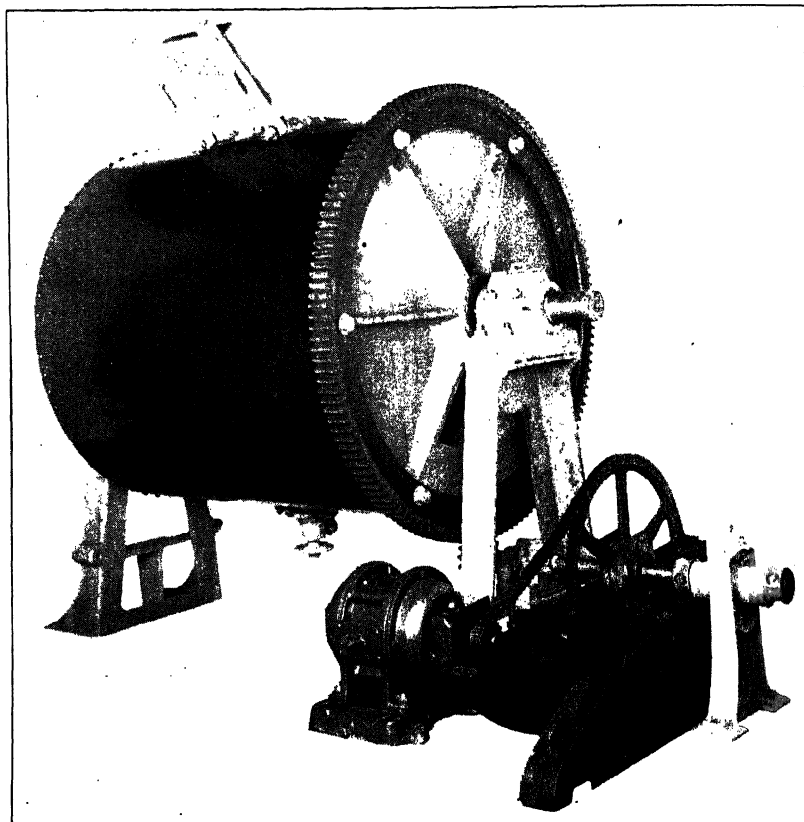


FIG. 15. Typical Pebble Mill.

pletely enclosed there is very little loss of volatile matter which occurs in all open types of grinding equipment.

**Pebble and Steel Ball Mills.** In Fig. 15 is shown the exterior of a typical pebble mill. Essentially these mills consist of a cylinder mounted so that by means of a gear drive the cylinder is caused to revolve. The interior of the cylinder is lined with blocks of buhrstone, porcelain, or special hardened steel. Inside this cylinder is placed a

charge of proper-sized pebbles or balls, which may be steel, porcelain, flint, or stone. If necessary, these mills can be water-jacketed for cooling.

Figure 16 shows a cross-sectional view of a loaded mill. At the top of the cylinder is the loading manhole, through which the dry material and vehicle are fed into the mill. When the charging is completed this manhole is closed by a cover, which is bolted down tight. Directly underneath, but on the other side of the cylinder, is the discharge outlet through which the finished material is drained off. Over this discharge outlet is a suitable grillwork to prevent the pebbles or steel balls from falling into the outlet valve.

The mill revolves at such a rate of speed that the pebbles are carried up on the side of the cylinder by centrifugal action, but only at a speed that enables the force of gravity just to overcome this centrifugal force and allow the pebbles to fall and roll over each other. Thus the material is subjected to a crushing and rubbing action by the impact of pebble on pebble, and the rubbing of pebble on the lining of the cylinder. This process is continued as long as is necessary to obtain the desired degree of dispersion.

In addition to the revolving speed of the cylinder there are several other factors which affect the operation of this mill.

(a) *Relation between pebble and material charge.* The mill usually is charged half full of pebbles. The volume of pebbles and material to be ground varies, depending upon the ease of dispersion. When the material is difficult to disperse, it is customary to hold the level of the material just above the pebbles. If the material is fairly easy to disperse, the mill can be loaded until it is about two-thirds full, although this usually increases the processing time. However, greater production per batch can then be obtained from the same mill capacity.

(b) *Consistency of material processed.* This usually is approximately the consistency of a thick soup or heavy cream. Naturally it

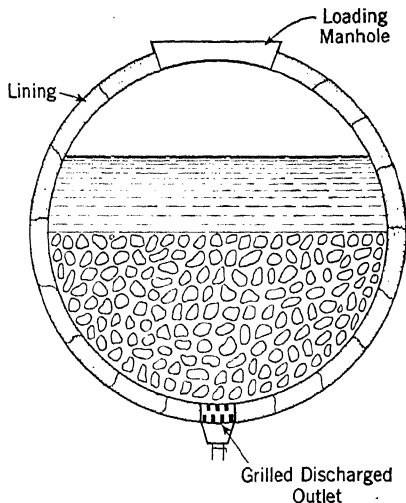


Fig. 16. Cross-Sectional View of Loaded Mill.

cannot be of any heavier consistency than will allow the pebbles to just move freely, and not be entrapped or float in the material mass. Likewise, if the consistency is too thin, the pebbles will rush through the mass of material too violently and cause excessive wear on the pebbles and the lining; also by striking each other and the cylinder lining too hard, small particles of foreign material from the lining and

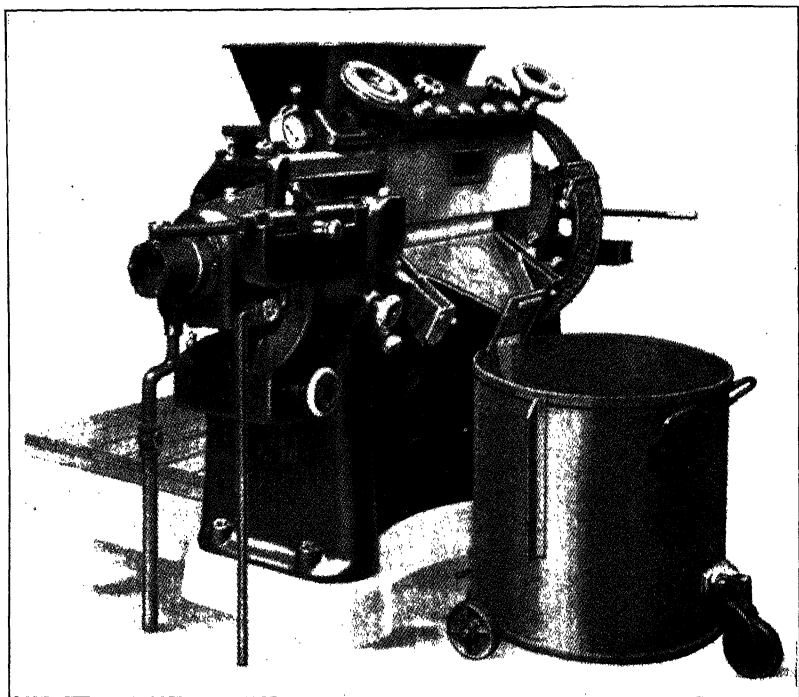


FIG. 17. Front View of Unroll Mill.

the pebbles will be introduced into the material, thereby contaminating it.

(c) *Pebble or ball size.* Pebbles or balls should be of such sizes and weight as to prevent them from floating in the material mass, and to obtain the maximum amount of grinding surface.

The pebble mill is generally used for processing pigments which are easy to disperse, buhrstone linings being used for house paints, flat paints, barn paints, etc., and porcelain linings for the better grades of enamels. Steel ball mills can also be used for all types and colors,

except white, and generally will turn out the same work in about half the time required on a pebble mill.

In this type of mill, mixing and grinding are combined in one unit of apparatus. Once the mill has been loaded and started running, it requires no further manual attention until it is to be discharged. Also, because it is completely enclosed, there is very little loss of volatile matter.

These mills do not require dressing of the grinding surfaces as do the stone or roller mills. However, in time the pebbles wear away

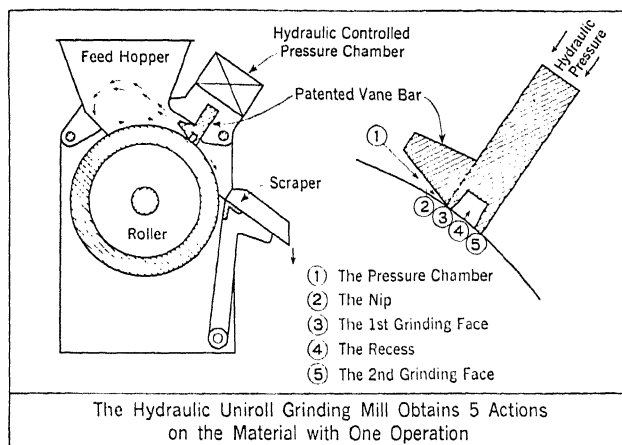


Fig. 18. Cross-Sectional Diagram of Uniroll Mill.

and are no longer efficient. Then they must be replaced. When the cylinder lining is worn out it is necessary to remove the worn lining and install a new one which is costly and at the same time puts the unit out of operation.

The pebble mills range in capacities from 25 gallons to 1,000 gallons.

**Uniroll Mill.** Figure 17 illustrates a typical uniroll mill. The mill is constructed so that a feeding hopper rests directly over the single hollow, water-cooled roll, which in addition to revolving also oscillates in a horizontal plane. Set against this roll is a water-cooled vane bar, as shown in Fig. 18. This vane bar is forced against the roll by means of hydraulic pressure, which is regulated by gage and can be maintained constantly at any pressure selected up to 750 pounds. It has two grinding surfaces, as shown in Fig. 18. These vane bars are constructed with four different angle sizes ( $5^\circ$ ,  $10^\circ$ ,  $15^\circ$ , and  $20^\circ$ ), which increase or decrease the size of the pressure chamber.



The premixed semi-paste is placed in the hopper and then the machine is started. Because of the revolving and oscillating action of the roll a violent agitation is imparted to the material. As the roll carries the material into the wedge-shaped pressure chamber, a wedge of paste is made which tries to force its way between the vane bar and the roll. Thus considerable pressure is developed against the vane bar, and a counter pressure almost as great must be applied by hydraulic means to the vane bar in order to resist this lifting action of the wedge of paste. Thus some of the material is forced past the nip and the first grinding face and is subjected to a severe rubbing action. After it has passed this first grinding face, the material enters the recess chamber, where it is further remixed before passing the second grinding face, where it must work against the vane bar pressure and get a second rubbing action. The material is then carried on the roll to the scraper knife, where it is scraped from the roll onto the apron.

These machines are equipped with rolls ranging from 10 inches in diameter and a length of 6 inches to 16 inches in diameter and a length of 26 inches.

These mills are quite flexible and are readily cleaned. The vane bar can be removed in a very short time, and the scraper blade can be very readily removed when worn and replaced with a new blade.

The mills require manual attention only to keep the feed hopper filled and to start the machine and regulate the hydraulic pressure on the vane bar at the start of operations. The apron is constructed so that the materials discharged from the ends of the roll are collected separately, because generally they do not have so fine a dispersion as the remainder of the roll surface. These ends must be manually returned to the feed hopper.

The consistency and viscosity of the semi-paste to be processed play a very important part in the operation of this mill. The vehicle must be such that there is a tendency for the paste to grip the roll, and material which does not do this should not be processed on this machine for best results. Furthermore, most efficient dispersion and rate of production are determined by the proper angle vane bar and grinding pressure. Thus for each formulation the proper consistency, the bar pressure, and angle of bar to be used must be determined for most efficient output and dispersion. When this has been done succeeding batches can be processed under similar conditions and similar results obtained.

The vane bars are equipped with relief holes which run through the bar from the recess chamber to the feed hopper. They are either plugged or kept open, depending on the pressure developed by the material in the recess chamber. If this pressure becomes too high we again have a tendency to lift the bar away from the roll, thereby decreasing the efficiency of dispersion. This pressure can be lessened by opening some of the relief holes. If the viscosity is very low it is essential to plug the relief holes in order to build up pressure. The number of relief holes to be plugged or kept open in the vane bar for the processing of any formulation must be determined in each case.

It is vitally important that this mill never be operated dry; otherwise the vane bar would tend to wear unevenly and, without any lubrication agent present, sear the face of the roll.

When the first grinding face has worn down to twice its original surface it is necessary to remove the bar and reface it to its original size. Usually a vane bar can be refaced three times. Beyond this is not practical because the size of the recess chamber is then so decreased that the mill no longer will operate properly.

These mills are used for making enamels, gloss paints, flat paints, etc.

**Colloid Mill.** In Figs. 19 and 20 are illustrated typical paste and liquid types of the Premier Colloid Mill. In the Premier Colloid Mill "rotor" A, as shown in Figs. 21 and 22, rotates within the confine of a "stator" B. The clearance between the working surfaces of the rotor and stator can be adjusted to as little

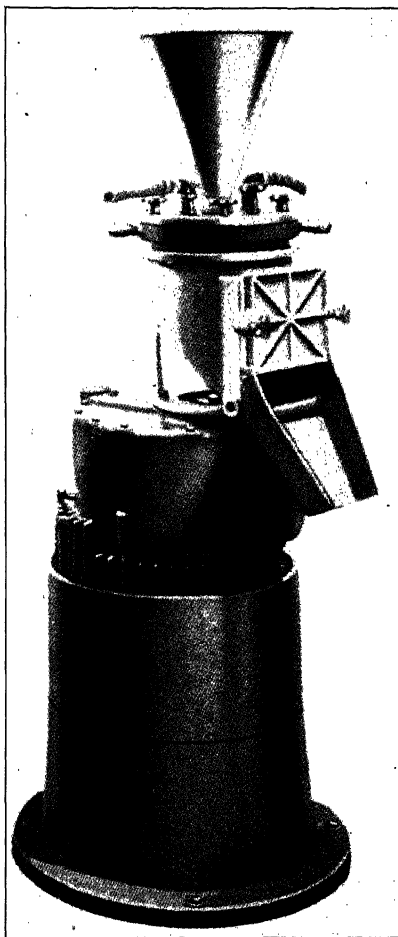


FIG. 19. Paste Type Mill, Direct-Coupled to Geared-up Motor.

as 0.001 inch. Thus material coming between these two surfaces is subjected to an intense hydraulic shearing action on a very thin film of material. The rotor is brought into position by means of an adjusting ring, and the distance between the rotor and stator is controlled by suitable gages for whatever clearance is desired.

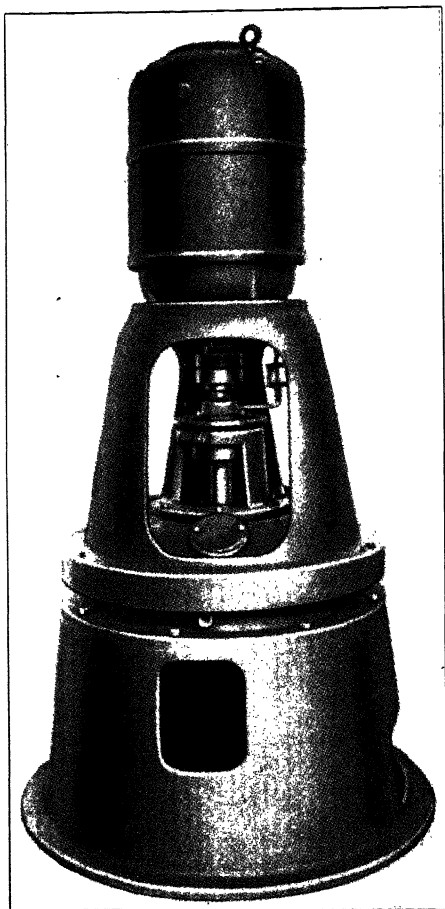


FIG. 20. Liquid Type Mill, Direct Coupled.

As material is fed into the mill it comes in contact with the rotor, and by centrifugal action the material is forced through the small annular clearance between the stator and the rotor. Here a working film is created when the material in contact with the rotor tries to

move as fast as the rotor and the material in contact with the stator tends to remain stationary. Between the two is the working film, which owing to the opposing actions tends to be torn apart. After the

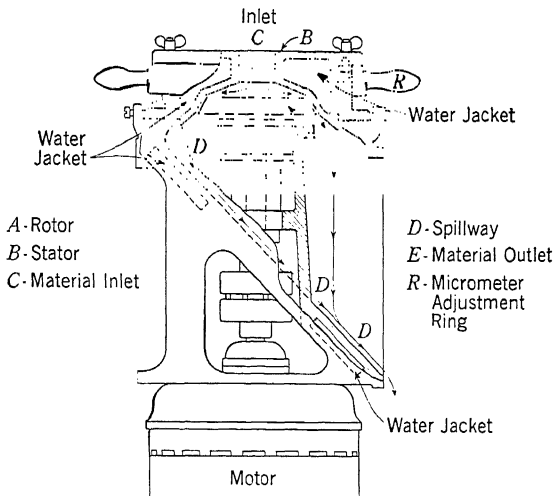


FIG. 21. Cross-Sectional View of Paste Type Mill.

material has passed the working surfaces it is discharged onto a spillway and from there is taken from the machine by means of the discharge outlet.

In the paste type mill, the material is fed from the top as shown in Fig. 21, whereas in the liquid type mill it is fed from the bottom as shown in Fig. 22.

The size and output of this mill is governed by the diameter of the rotor. In the paste type mills these range from 3 inches to 12 inches. In the liquid type mills they range from 10 inches to 20 inches.

Viscosity of the vehicle and the adhesion of the mixed material to the working surfaces play a very important part in the functioning of this mill.

Since most of the work is done by the material working on itself, there is very little wear on the rotor and stator, and the machine

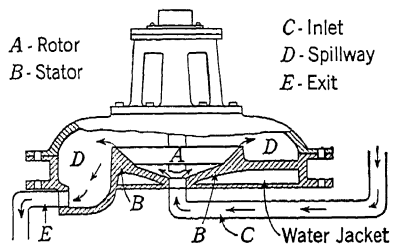


FIG. 22. Cross-Sectional View of Liquid Type Mill.

can be run 12 to 24 months without any regrinding of the working surfaces.

The machine can be readily cleaned by passing a suitable cleaning liquid through the machine and thereby washing it clean. Because of this, the setting of the machine need not be changed at the end of a day's run.

This type of machine can be used to process free-flowing enamels and paints. A material having too high a viscosity cannot be handled because of the large amount of heat which would be developed and the requirement of an excessive amount of power.

Following are the characteristics of a typical-sized mill:

	Paste	Liquid
Rotor size—_inches	6	10
Horsepower of motor	10	25
Mill speed—r.p.m.	9,000	3,600
Floor space—_inches	17×17	23×23
Capacity—gallons per hour	50–100	50–600

From the descriptions of the foregoing types of dispersion and grinding equipment it is readily appreciated that no one type of machine is a "cure-all." All types have their use and place in the industry. Kind and quantity of material to be produced, size of plant and space available, the economic condition of the manufacturer, all these control what types, capacities, and numbers of the various machines should be installed to give the most efficient and economical operating performance. The variety of material to be manufactured and the size of the batches processed directly control the selection of machines.

It should be noted that paste processed on a stone, roller, uniroll, or colloid mill may be used at any time without waiting for the entire batch to be finished. In the bramley, pebble, or ball mill, the entire batch must be completed before any of the batch can be used.

### **Mills Selection and General Performance Data**

In considering what type of mill to use, the following questions should be carefully considered:

1. Does the machine disperse the material to the degree desired by the purchaser?
2. Does it meet production requirements?
3. How much floor space is required?
4. How much horsepower is necessary to operate the machine?
5. Is it flexible enough to fit particular problems?
6. What repairs and upkeep are necessary to keep the machine operating efficiently?
7. What is the initial cost of the machine?
8. What is the length of life of the machine?

Since the performance output of the various mills varies with the type of material being processed, we are listing typical performance rates.

From the New York Paint and Varnish Production Club paper of 1934 on pigment dispersions, we have the following data on a paste consisting of 70 per cent Titanox C and 30 per cent varnish:

Type of Mill	Hp.	Lb. per Hr.
30-in. tandem buhrstone mill	6½	245
30-in. single buhrstone mill	3½	128
26-in. tandem buhrstone mill	4¾	156
26-in. single buhrstone mill	2¾	80
20-in. single buhrstone mill	2	58
12- × 30-in. three-roll mill	6	210
50-gal. buhrstone-lined pebble mill	2	48
Five-roll mill	10	1,175
Banbury (production)		156
Colloid mill (prod. size) clearance 0.005 in.	1½	120
clearance 0.010 in.	1½	328

Typical performance factors for various types of products are listed on page 750.

## Thinning

After a paint has been ground in a semi-paste form, it is necessary to incorporate it with the remainder of the vehicle to produce the ready-mixed product. This is usually called “thinning,” and is described in detail in Chapter 24.

## 750 PAINT MIXING AND GRINDING OR DISPERSION EQUIPMENT

Type of Mill	Floor Space	Hp.	Rpm.	Capacity Finished Material Gallons per Hr.
<i>House Paints</i>				
36 in. Single Stone	4 × 4 ft.	7½	34	75-90
6 × 5 ft. Pebble	10 × 11 ft.	20	19	80-90
130 gal. Bramley	6 × 9 ft.	15	38	75
12 × 30 in. Three Roll	5½ × 10 ft.	20	300	200-250
<i>Flat Wall Paints</i>				
36 in. Single Stone	4 × 4 ft.	7½	34	70-80
6 × 5 ft. Pebble	10 × 11 ft.	20	19	80-90
130 gal. Bramley	6 × 9 ft.	15	38	80
12 × 30 in. Three Roll	5½ × 10 ft.	20	300	160-200
<i>Semi-Gloss Paints</i>				
30 in. Shingle Stone	3½ × 3½ ft.	5	42	20-25
6 × 5 ft. Pebble	10 × 11 ft.	20	19	25-30
130 gal. Bramley	6 × 9 ft.	15	38	30-45
12 × 30 in. Three Roll	5½ × 10 ft.	20	300	50-65
<i>Gloss Paints</i>				
26 in. Single Stone	3 × 3 ft.	5	42	5-10
6 × 5 ft. Pebble	10 × 11 ft.	20	19	30-40
130 gal. Bramley	6 × 9 ft.	15	38	40-60
12 × 30 in. Five Roll	5½ × 11 ft.	20	300	15-40
12 × 30 in. Three Roll	5½ × 10 ft.	20	300	25-50
<i>Enamels</i>				
20 in. Tandem Stone	2½ × 5 ft.	5	44	5-10
6 × 5 ft. Pebble	10 × 11 ft.	20	19	20-25
130 gal. Bramley	6 × 9 ft.	15	38	15-35
16 × 26 in. Uniroll	8 × 5 ft.	20	210	10-20
12 × 30 in. Five Roll	5½ × 11 ft.	20	300	10-25
12 × 30 in. Three Roll	5½ × 10 ft.	20	300	40-50

## ACKNOWLEDGMENTS

The author wishes to thank Charles Ross & Son Company, Kent Machine Works, Bramley Machinery Corporation, Abbé Engineering Company, Keenock Company, Ltd., and Premier Mill Corporation for their help and cooperation in assembling the data and illustrations used.

*Editor's Note:* There are equipment manufacturers other than those mentioned who also make satisfactory standard and special mixing and grinding equipment.

## CHAPTER 24

### THINNING, TINTING, SCREENING, FILTERING, FILLING, LABELING, AND PACKAGING

AUSTIN O. ALLEN

The operations of thinning, tinting, screening, filling, labeling, and packing are largely mechanical, and marked improvement has been made in the modernizing of such operations in the paint industry.

Although the paint industry in general may be said to be less progressive in mechanizing than many other leading industries, in these particular operations it is following to a large extent the modern trend of line production and larger and speedier mechanical units.

#### Thinning

The thinning operation consists of adding the necessary vehicles to the previously ground mill base (paste) to produce the finished paint. Mill bases are sometimes ground and stored in paste form to be used as needed. When this method is followed precautions should be taken to prevent the paste from skinning. This is sometimes accomplished by storing the paste in sealed containers. A convenient and economical method is to lay lightweight lacquer-sized paper over the surface of the paste to exclude air. The type and size of container for storing paste will depend upon the method of storing and handling as well as the quantity of paste to be stored. The handling of containers is sometimes accomplished by trucks and sometimes by means of electric hoists and monorail conveyor.

The type and size of reducing tank will depend on the quantity of paint to be reduced at one time. The tank should be located on the floor below the paste storage so that the paste can be dropped through a chute by gravity. Where this is not possible the paste is sometimes transferred to the reducing tank by means of an electric hoist. The reducing tank is equipped with an efficient agitator to mix the paste and vehicle properly. The so-called change can mixer (Fig. 1) is often used for reducing small batches (up to 150 gallons). Large reducing tanks are usually stationary and range in size from 200 to 2,000



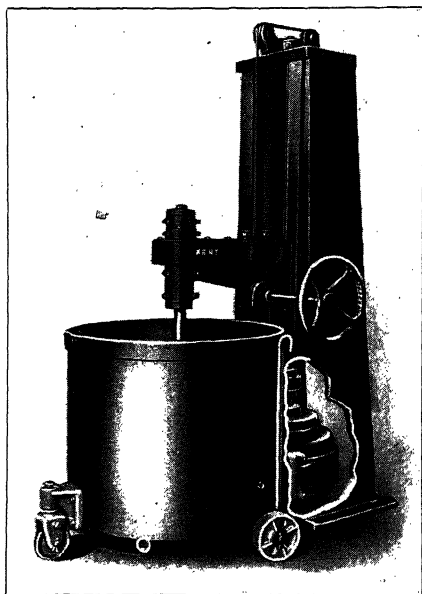


FIG. 1. One Type of Change Can Mixer.



FIG. 2. An Installation of Stationary Tanks.

gallons capacity (Fig. 2). Some plants use portable reducing tanks (equipped with agitators) ranging from 200 to 1,000 gallons. These tanks are usually moved by means of electric lift trucks to the loading and unloading locations.

The vehicle to be added to the batch can be either weighed or measured. A convenient method is to have a central weighing tank so located that the various oils, varnishes, and thinners can be pumped

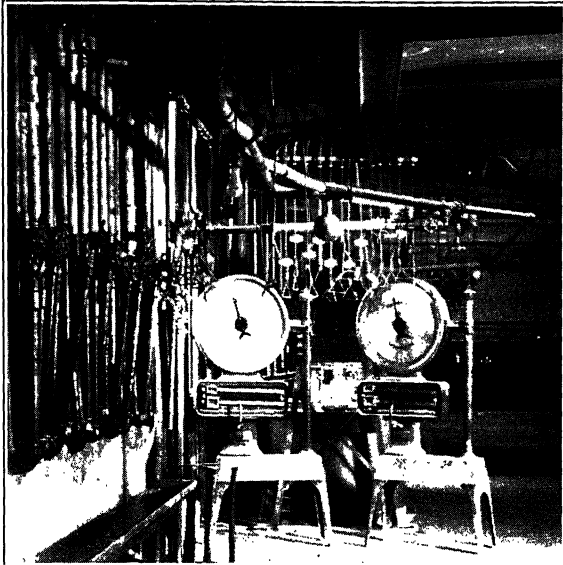


FIG. 3. An Installation of a Central Weighing Unit.

or can flow by gravity (Fig. 3). When the desired amount of vehicle has been weighed into the tank, it is either pumped or flows by gravity to the reducing tank.

### Tinting

Practically all batches of paints require tinting. Even white paints are usually tinted slightly with blue or purple toner to improve the color. Light tints are usually made from white paints. Deep shades and solid colors are made from the proper-colored pigments so that the minimum of tinting will be required.

Tinting pastes should be ground in a vehicle with a high solid content and should be adjusted to standard strength. Care should be taken to avoid skinning. When these precautions are taken and care-

fully weighed amounts of tinting pastes are added to the batch, the time required for tinting will be greatly reduced. The batch must be compared to the standard for color and adjusted if necessary by the addition of required small amounts of tinting paste. When a paint is being tested for color, it should be applied in the same manner in which it is to be used. The final approval of quality and color should be made in a properly equipped control laboratory under the supervision of a qualified paint chemist.

Maintaining color standards accurately has always been a troublesome problem for the paint technician. Considerable attention has been given to this problem, but no entirely satisfactory method has been developed. Several types of spectrophotometers have been developed in recent years. The difficulty so far is that either the price of such equipment is too high or the amount of time required to make a color comparison is too long. The five methods that are most commonly used for keeping color standards are:

1. Wet samples of the paint.
2. Wet samples of the color in special vehicles.
3. Dry panels of the color.
4. Porcelain color panels.
5. Spectrophotometer curves.

### Screening

The screening of paints can be simplified if careful control is exercised over the quality of grinding and over the elimination of skins as well as proper filtering of vehicles. Many manufacturers use various grades of fabrics, such as cheesecloth, muslin, and felt for straining the various grades of paint. Probably the most widely used and quite satisfactory method is the vibrating screen shown in Fig. 4 with wire cloth of the desired mesh. The mesh which has been found satisfactory is:

- Flat white and exterior house paint—24–40 mesh.
- Interior gloss paints—50–80 mesh.
- Interior enamels—100–120 mesh.
- Industrial enamels—140–200 mesh.

### Filtering

Screening is often unsatisfactory for certain high-grade finishes, for example, automotive finishes and refrigerator finishes. In such cases a variable-speed centrifugal clarifier shown in Fig. 5 is used.

Clear vehicles are clarified by means of a centrifugal clarifier or filter press. The centrifugal clarifier is usually satisfactory for architectural varnishes and for vehicles used in many grades of paints and enamels for architectural use. Many industrial varnishes and vehicles for high-grade enamel finishes must be clarified by means of a filter press. The two types of presses in most common use are the plate

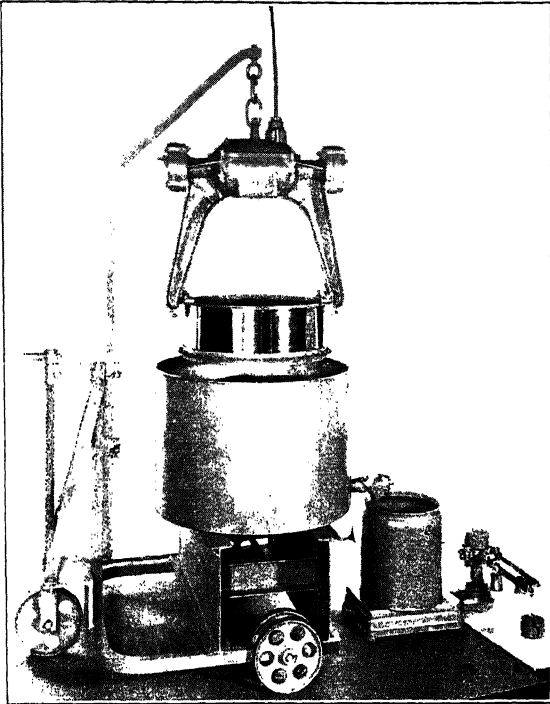


FIG. 4. Portable Vibrating Screen Unit.

press and the seitz filter. Many types of filtering medium can be used on these presses. It is advisable to secure the recommendations of the equipment manufacturer. Figures 6, 7, and 8 illustrate these types of equipment.

### Filling

Filling equipment has been improved in recent years to such an extent that it can be used economically in most paint plants. Many filling machines are easily adjustable for filling  $\frac{1}{32}$ -gallon to 1-gallon

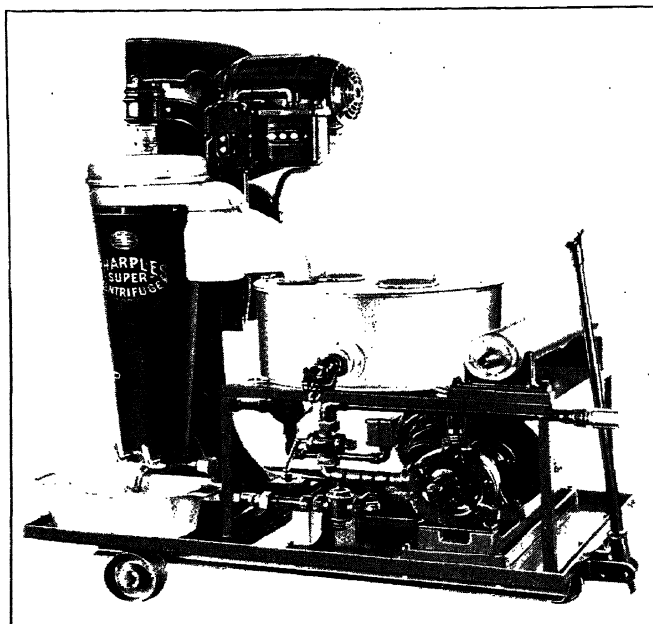


FIG. 5. Variable-Speed Centrifugal Clarifier.

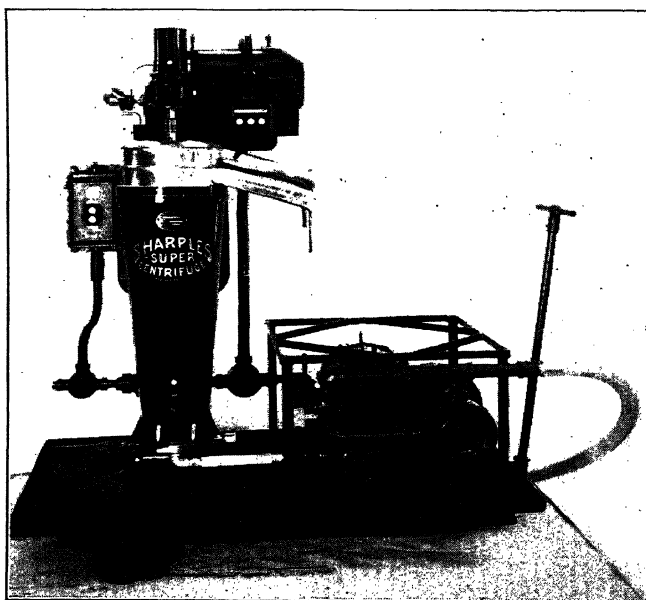


FIG. 6. Varnish Type Centrifugal Clarifier.

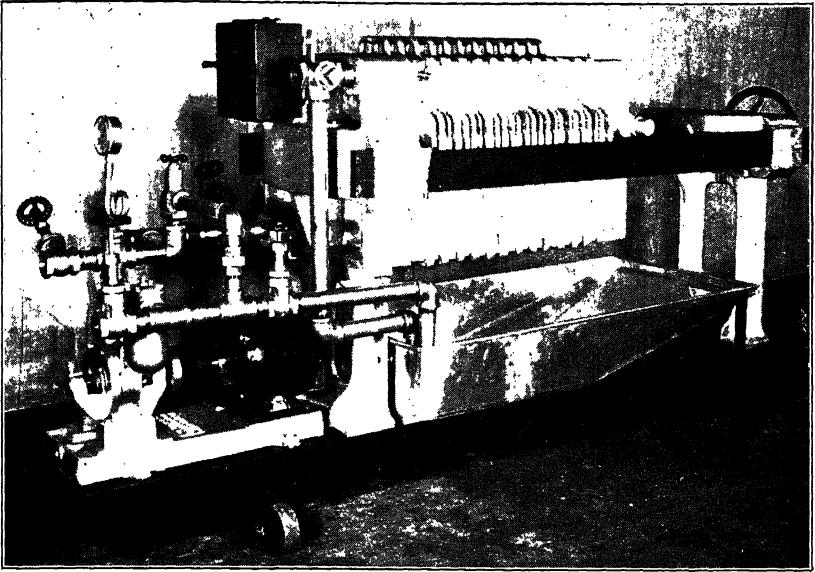


FIG. 7. Plate and Frame Type Filter Press.

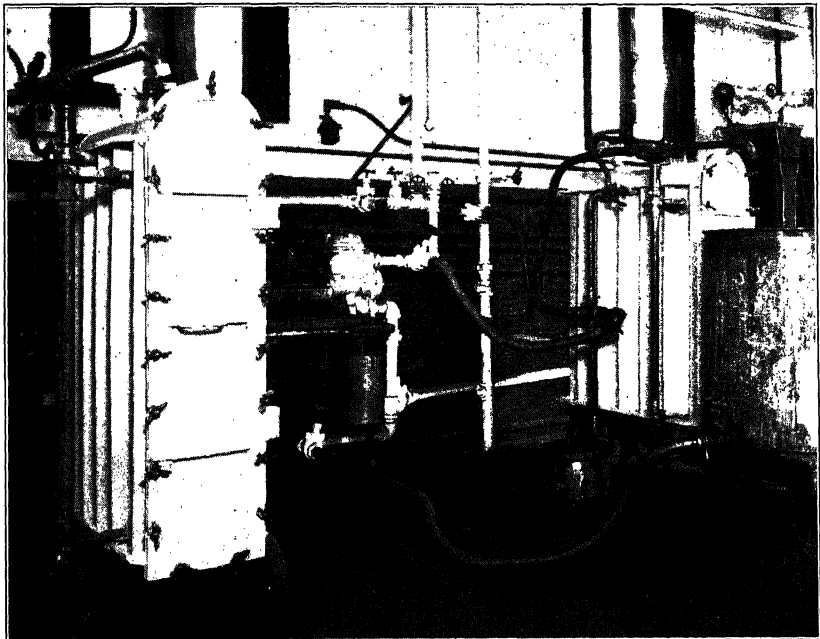


FIG. 8. Seitz Filter.

containers. Many machines have two or three operating speeds. This permits the filling operation to be conducted at the speed best suited to the particular plant conditions. Figure 9 shows a filling machine which is capable of filling 12 to 18 1-gallon cans per minute, 18 to 25  $\frac{1}{2}$ -gallon cans per minute, and 25 to 30 smaller sizes per minute. The filling is controlled by a foot-operated clutch which can be

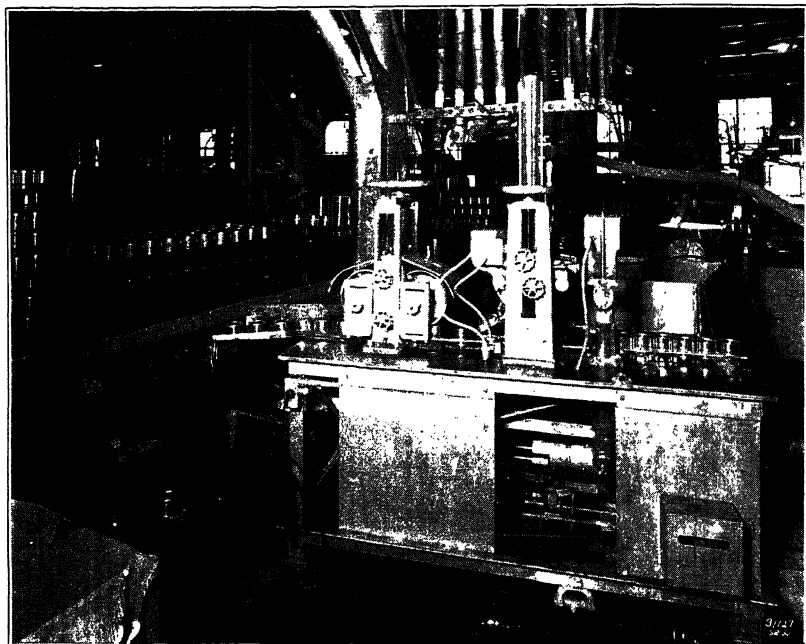


FIG. 9. Single Can Filling and Closing Machine.

engaged for each container or can be locked in position for continuous operation. This equipment is designed so that it will operate from tanks on the same floor or from floors above. An automatic cover dropper is built into this filling unit so that the filled and sealed cans are delivered to a conveyor line. This complete equipment is mounted on rubber-tired casters and can be moved easily from one tank to another.

Multiple-filling machines are now available which have a capacity of approximately 40 1-gallon or  $\frac{1}{2}$ -gallon cans per minute and 80 to 120 smaller-sized cans per minute. This type of filling machine is shown in Fig. 10. It should be connected by conveyor to an automatic closing machine (Fig. 11).



FIG. 10. Multiple-Can Filling Machine.



FIG. 11. High-Speed Automatic Closing Machine.



It is possible to arrange the filling operation so that a minimum amount of time is necessary for cleaning the filling equipment. This can be done by arranging the order of filling so that different batches can follow from white and very light tints to the darker colors. In such a procedure, it is necessary only to flush out the machine with thinner. This requires only a few minutes. Thorough cleaning, which is necessary when changing to a decidedly different color or at the end of the day, takes one-half to one hour.

Greatest benefits can be derived from automatic filling if careful planning is done so that the largest possible quantity is filled at one time. It is also advisable to fill consecutively as many cans of a single size as requirements will permit. Such planning will usually justify machine filling in comparatively small plants. It is generally conceded that automatic filling is economical in minimum lots of 100 1-gallon cans, 200  $\frac{1}{2}$ -gallon cans, 400  $\frac{1}{4}$ -gallon cans, and comparable amounts in smaller sizes.

Although automatic filling is economical in most paint and varnish plants, it is always desirable to give consideration to selection of the type of equipment best suited to the existing conditions. The handling of cans to and from the filling machine should be considered at the same time. Equipment manufacturers will usually supply engineering service for properly planning the most efficient installation.

### Labeling

The installation of equipment for economical labeling will depend on the volume of material and the sizes of containers to be labeled. Even in small plants a labeling machine will usually effect an economy. Labeling machines are available that can be adjusted to label all sizes from  $\frac{1}{32}$ -gallon cans to 1-gallon cans. Figure 12 shows a labeling machine installation well arranged for hand filling.

No hard and fast rule can be set to establish the volume of production necessary for economical line operation. However, for economy it is advisable to have the labeling operation follow directly after the filling to avoid intermediate handling. When the volume is not sufficient to justify a separate line for filling and labeling a single-sized can, it is possible to have the conveyor line from the filling lead to two labeling machines so that the cans can be diverted to either labeling machine. With this arrangement it is possible to adjust one labeling machine for a given size while the other machine is labeling another size. In this way practically an uninterrupted operation can

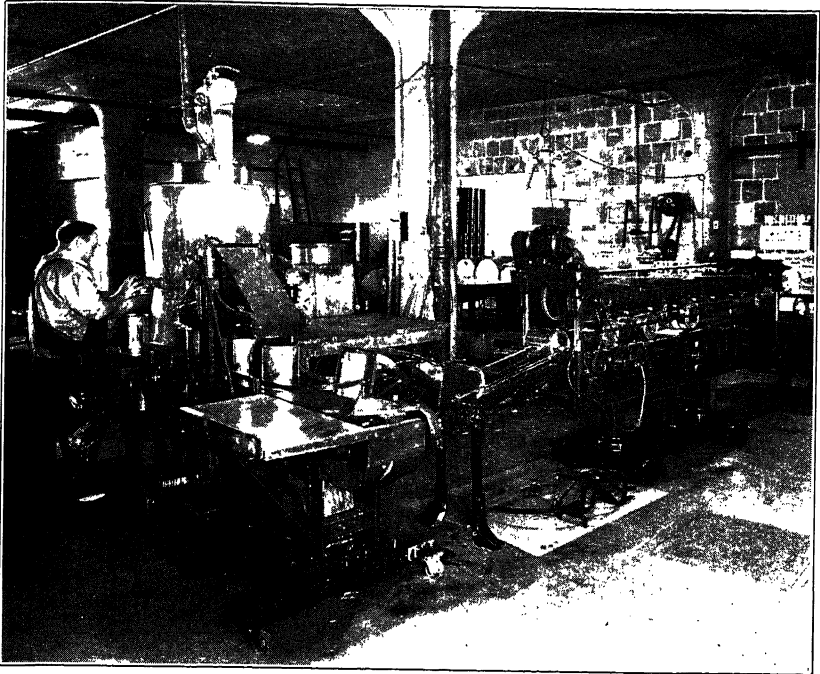


FIG. 12. Installation of Labeling Machine for Small to Medium Volume.

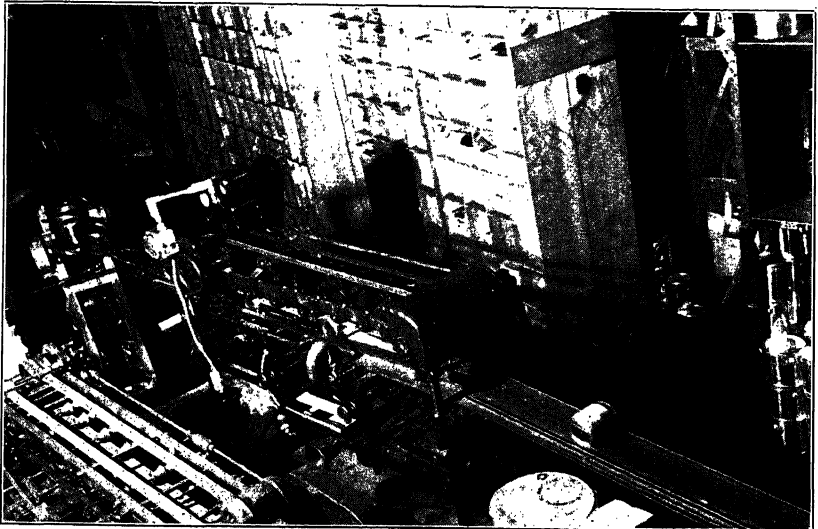


FIG. 13. Installation Showing Two Labeling Machines Fed from One Conveyor Line.

be maintained. Figure 13 shows such an installation that can handle 4,000 to 8,000 cans per 8-hour day.

Figure 14 shows an installation of four labeling machines which are so arranged that different sizes are labeled on the different machines and the labeled cans discharged to a conveyor for casing. This type of installation avoids the necessity of frequent adjusting of the machines for various sizes.

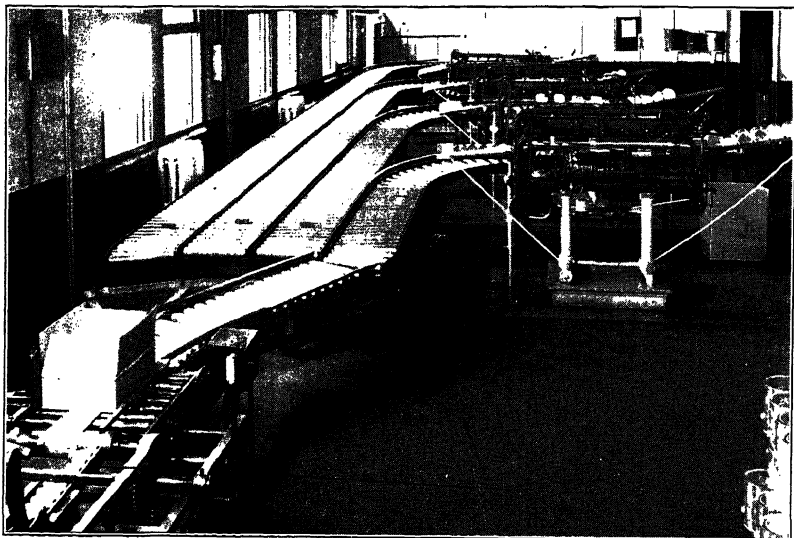


FIG. 14. Installation Showing Four Labeling Machines Leading to One Sealing Unit.

It is sometimes desirable to label the empty cans, and do the filling later. The same equipment is required, the only difference being the arrangement of equipment.

### Packing

Packing and sealing equipment is available for almost any desired volume. It is very difficult to make any general statements regarding the economy of any particular installation because so many factors are involved. A survey should be made of each individual plant, taking all factors into consideration. Such engineering service is available from the equipment manufacturer. The gluing and compression units are being used profitably in many plants. They are very easily and quickly adjusted for all carton sizes, and can be connected into

a conveyor line in such a way that an operator can fill the cartons direct from the labeling machine. The sealed cartons are discharged onto the conveyor line leading to the stockroom, as shown in Fig. 15.

Figure 16 shows a gluing and compression unit installed in such a way that two operators can attach bales to 1-gallon or  $\frac{1}{2}$ -gallon cans and insert the cans in unsealed cartons. The cartons then pass through

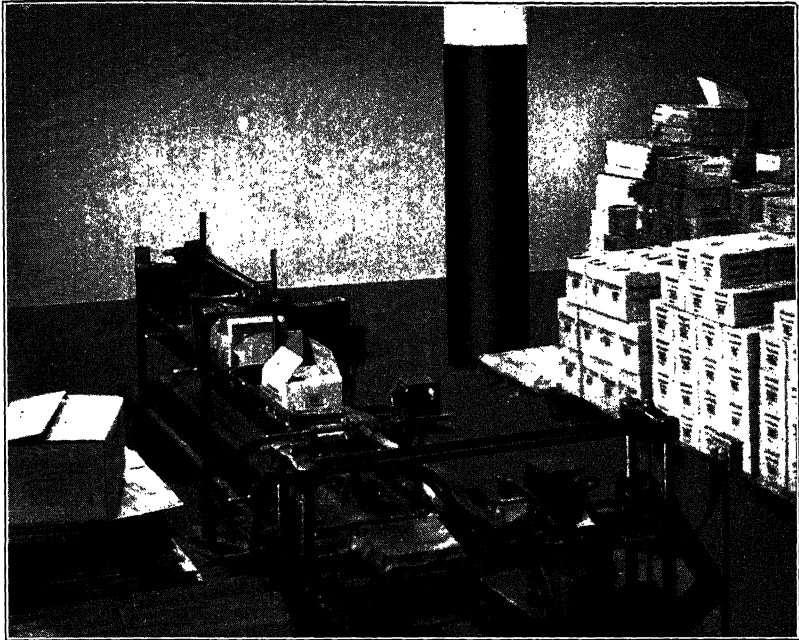


FIG. 15. Installation of Gluing and Compression Units Capable of Handling 100 to 150 Cartons per Hour with One Operator.

the gluing machine where the top and bottom flaps are glued, then into the compression unit where the cartons are held under pressure long enough for the glue to set. The capacity of this installation is a minimum of 500 cartons per hour.

Self-adjusting automatic gluing and compression units are available for installations where it is desirable to pass cartons of various sizes through the gluing and compression units simultaneously. For instance, two, three, or even more labeling machines can be operated at the same time on different-sized containers and the filled cartons discharged to a single conveyor leading to the self-adjusting gluer and compression units, as shown in Fig. 17 and Fig. 18.

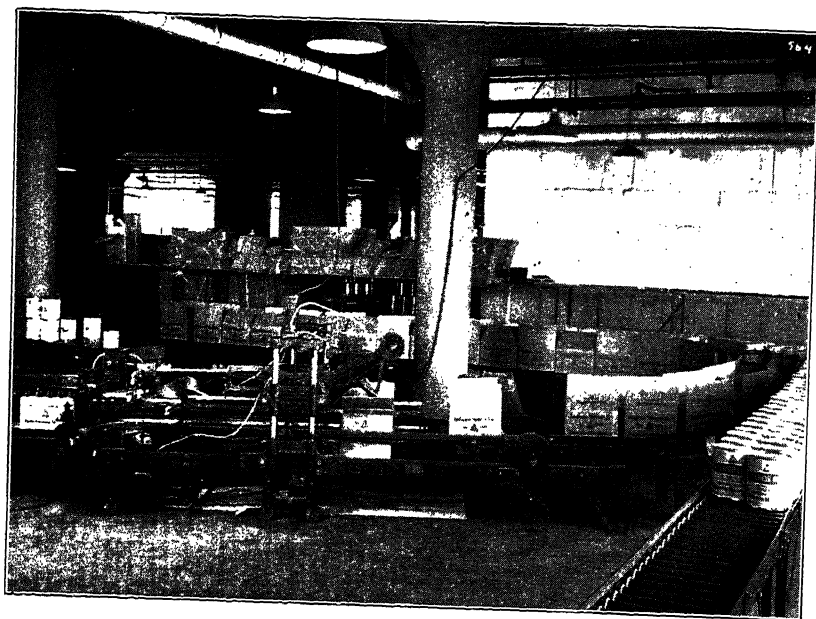


FIG. 16. Installation of Gluing and Compression Unit Capable of Handling 500 to 700 Cartons per Hour.

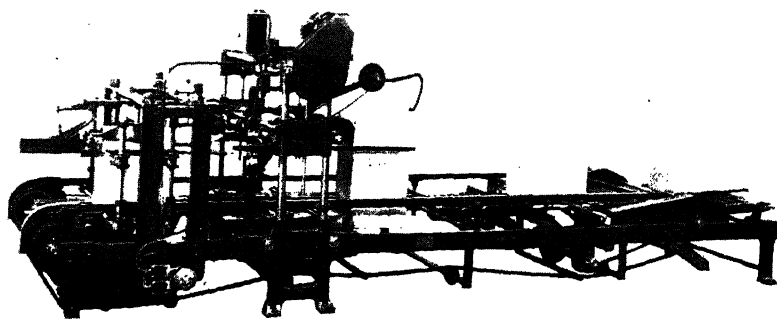
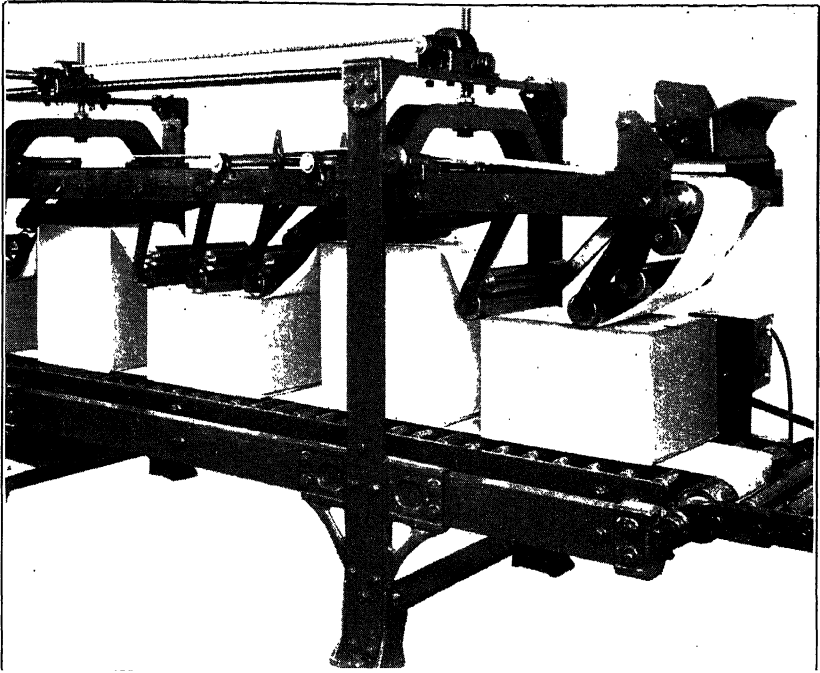


FIG. 17. Self-Adjusting Automatic Gluer for Gluing Various Size Cases.



18. Self-Adjusting Compression Unit.

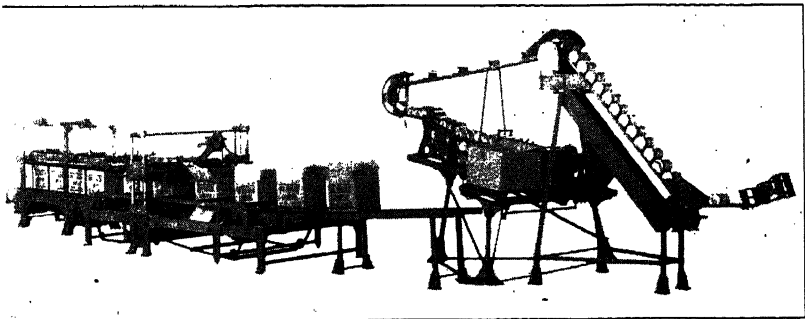


FIG. 19. Automatic Case Filler, Gluer, and Compression Unit for High-Speed Packing.

Where high-speed fully automatic packaging is advisable an automatic packer such as is shown in Fig. 19 can be installed between the labeling machine and the automatic gluer. A completely automatic installation of this type is advisable only when the volume is large enough for continuous operation on a single size.

The foregoing descriptions make it obvious that some combination of automatic filling, labeling, and packing can be designed to fit the volume and other existing conditions in almost any plant. The economy of such installations can be easily and accurately predetermined.

#### ACKNOWLEDGMENTS

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# STAINS





## CHAPTER 25

### THE FORMULATION AND USES OF STAINS

WILLIAM H. PEACOCK

Staining was one of the skilled crafts of ancient times. Tribal totem poles and arrow marks, "medicine" beads, masques and regalia, mummy cases, skins and pelts for tents and clothing are examples of early stain applications. An interesting linkage with the present day is the similarity of the "war-paint" stains of the savages, the medieval age coats-of-arms, the walnut skin stains of Aryan spies, and even the black-face cosmetics used by the modern raiding "commandos."

In our day, however, stains have importance not only for war, decorative, and identification purposes, but also for economic and technical purposes. For instance, it has become an economic necessity to stain the readily available woods to duplicate the appearance of species less abundant and higher in cost. Again, when we desire to color a run of paper board only on one side, we use stains and colored coatings. The industrial uses of stains are multitudinous and varied. Stains are used on cotton osnaburg and burlap (for military purposes). This is a list of miscellaneous uses: cleaners, polishes, feathers, cat-tails, straw and other grasses, plastics, jute, horn, and ivory, floor tile, advertising novelties, lacquered handbag and picture frames, agricultural seeds, fruit, feeds, and as animal branding inks. Art and handicraft objects of many kinds also are stained.

#### MAJOR TYPES OF SURFACE COLORING

Surfaces are colored by three general types of decoration: painting, dyeing, and staining. When a colored coating, usually resinous, is applied to the surface the process is called painting, or, if the coating is uncolored, it is often called coating or glazing. When the material is permeated by dyes that may penetrate sufficiently to color much of the interior, the process is called dyeing. When the colored effect is produced only on or in the surface layers, particularly when a minimum amount of binder is used, the process is called staining. It should

be noted, however, that while certain craftsmen, particularly wood-stainers, carefully differentiate these three coloring processes, in the lacquer and varnish trades, dyed lacquers and dyed varnishes are called lacquer stains and varnish stains respectively. Another well-known exception to be noted is so-called stained glass, which is usually fire-glazed or processed. Printing is a special type of painting or staining.

### **Definition of a Stain**

A stain, therefore, may be defined as a solution or suspension of coloring matter in a vehicle, designed primarily to be applied to the surface of articles to impart color effects, rather than to form a protective coating. The coloring matter may be as varied as berry juices, ground clays, and synthetic dyes. The vehicle may be a liquid, emulsion, paste or solid, with or without binders or coating materials present. The distinction between a stain and a paint lies in the fact that most of the stain vehicle does not remain as a protective coating.

## **HISTORY**

### **The Evolution of Stains**

Staining procedures today differ from those practiced by the ancient craftsman, especially in the types of stains used. Evolution in the art has been along the lines of the development of new dyes, new vehicles, and new methods of application. Most of the advances have occurred during the last half century.

### **The Evolution of Staining Colors**

Some of the coloring agents used by the older artisans in staining and dyeing are in use today in various arts, although many of them are now made synthetically. Their antiquity may be realized better by citing a few examples given by Dubonnet (11, 28) and others. Moses mentioned "Tola," which was cochineal, an insect product. Dioscorides mentioned its use in Greece also (25 B.C.). Long before that (2500 B.C.) the Chinese used vermilion (red mercuric sulfide). A blue used by the Egyptians since the fourth dynasty is reported as copper oxide, while a copper carbonate was their "Azzuro," and Ultramarine Blue is still to be seen on old monuments on the upper Nile.

Woad was one of the earliest dyes of China and Europe, as was the indigo of India and Egypt. The Assyrians used a natural blue smalt,

as did later workers until after its commercial synthesis was begun in Saxony in 1538. Tartary sent lapis lazuli into commerce at the handsome value of \$20 an ounce. Before 1000 B.C. regal Tyrian purple was obtained from Mediterranean mollusks. Mangin from mango-fed Bengal cows, and safflower, turmeric, and Persian berries came from the Orient. Turkey and Holland contributed madder (natural alizarine), while from the Azores and Africa came litmus, archil, and other lichens. Undoubtedly, a great miscellany of fruits, berries, teas, brews, dyewoods, peats, asphalts, tars, colored clays, and powdered rocks were used and obtained from local sources.

The discovery of the Americas opened up the supply of dyewoods from the West Indies and South America, and Mexican cochineal (1492-1518). Logwood, fustic, osage orange, and the soluble and insoluble redwoods were all used, and are still in use today. Awakening science brought out prussian blue (1710), indigo extract (indigo sulfonate, 1740), and picric acid (trinitrophenol, 1788), and all for years were used in stains.

The wood stainers, particularly, used other products of the growing inorganic chemical industry, notably ammonia, permanganates, and bichromates. And, finally, after Perkins' famous work with mauve in 1856, the rise of the synthetic dyestuff industry placed in the hands of the stainers the hundreds of organic dyes and derivatives available today. In addition, therefore, to all the better pigments and dyewoods of antiquity we have available all the colored salts, mordants, synthetic dyes, and coloring aids of modern chemistry. A tabulation and excellent bibliography covering literature from 1685 to 1923 on the chemical constitution of many of the ancient and modern coloring matters is to be found in the Colour Index (6).

A chronological tabulation of the various periods in coloring would be substantially as follows:

Use of natural materials—Earliest history to A.D. 1538.

Increasing use of dyewoods (notably logwood)—A.D. 1492.

Use of synthetic duplications of natural earths and stones—A.D. 1538.

Use of synthetic inorganic reagents and mordants—A.D. 1710.

Increasing use of synthetic organic dyes—A.D. 1895 to date.

There are to be found no sharp demarcations between these periods. Dissemination of trade knowledge was slow, many formulas being disclosed only by father to son. Accordingly, the production, distri-

bution, and adoption for use of new materials were always a gradual development over long periods.

### THE PROPERTIES OF COLOR

Before discussing the coloring agents used in modern stains, it may be proper and informative to review, somewhat briefly, the nature of color as a physical phenomenon, some of the factors that influence the production of color effects, and the phraseology used by professional colorists.

#### Why Coloring Agents Appear Colored

Color is a phenomenon of light, and, although the nature of light has not been established definitely, it seems to be a wave form of energy (16). When these energy waves, approximately 400 to 700 millimicrons in length, reach the retina of the normal human eye, we get the psychological response, experience, or sensation of light, with or without color. If sun waves from throughout the whole of this relatively narrow band reach the eye unchanged, the response produced is known as "white" or white light. If, however, these waves are strained, as it were, through a wave trap to eliminate in whole or in part some of the waves and transmit others, the response obtained will vary with the several wavelengths and amount or intensity of energy received. Coloring agents, therefore, are merely convenient wave traps, and "tune" the light beams, as it were, much in the manner that radio receivers select broadcasting bands and stations.

None of the coloring materials on the market today are "sharp tuners," restricting the light transmission to any one wavelength, for all transmit light over a wide range. For example, yellow dyes usually transmit some color at each wavelength throughout the whole range, passing about 0.8 per cent of the incident energy having a 400-millimicron length, rising to 20 per cent at 515 millimicrons, and to 70 to 82 per cent of the incident energy at 550 to 650 millimicrons. For reasons not entirely understood, the mechanism of the optic system of human beings registers this series of transmissions as a sensation we call yellow. Physicists have integrated mathematically the energy transmission of yellows and find they have a "dominant wavelength" in the neighborhood of 570-590 millimicrons (14). Similarly for other color responses the dominant wavelengths are close to those listed in Table I.

TABLE I

## DOMINANT WAVELENGTH RANGES

Red .....	700-610	millimicrons
Orange .....	610-590	"
Yellow .....	590-570	"
Green .....	570-500	"
Blue .....	500-450	"
Purple * .....	450-400	"

It is a matter of importance for the progressive stainer and student to note that an international color commission (20) has coordinated and standardized the recording and integration of spectral transmission and reflectance data so that a color effect can be expressed mathematically in terms of standard tri-stimulus values. These values have been related to psychological responses through the fact that experiments indicate the three calculated theoretical stimuli would reproduce the same color response as viewing the actual dye effect. It takes special training and equipment to interpret and use this physical method of colorimetry. Nevertheless, its use is growing, and a study of these methods is strongly recommended to all colorists. It may be noted in passing that this is the physicists' conception of color. Manufacturing dye chemists view color as the resultant of chromophoric groups in chemicals (8), and a third viewpoint on color is that of the psychologists with reference to the stimuli that give rise to color responses.

### Factors Influencing Color Effects

There are many factors, some obvious, but many little known, that affect the color obtained with stains. The practical stainer is careful to compensate for them, either consciously or through the routines of experience. Some are purely optical phenomena, others are chemical or mechanical. Among these may be discussed the following as being of major importance:

**Transparency, Translucency, Opacity (Effect of Ground Color).** When in solution or finely dispersed in transparent media, most of the soluble dyestuffs are transparent or (occasionally) translucent. Accordingly, the original or self-color of the material to be stained

\* Many color physicists call the whole spectral region below 500 the "blue end," and avoid using the terms purple or violet for the region 400-450 millimicrons. Usually purple color effects are really "minus green" rather than just violet light, so that their dominant wavelengths are often written as greens preceded by a minus sign.

will "show through" and is a factor or ingredient of the final color effect. For example, a bright transparent yellow stain will appear yellow only when applied to a colorless, white, or light-colored object, and will be practically without visible effect if applied to a black object. Dark-colored objects, therefore, can be restrained to light hues only by first applying one or more opaque white or light-colored "ground" or masking coats. On the other hand, an object with a yellow self-shade can be stained green by applying a green or blue stain, or can be stained brown. Many other examples are listed in Table VI. Finally, it should be noted that transparency has a profound effect on gloss.

**Film Thickness.** Stains applied as transparent films will vary in tinctorial strength in a mathematical relationship to the thickness of film applied. Doubling the film thickness will nearly double the color strength in most cases. This phenomenon is particularly noticeable when sags or pools are formed, as in a coating; or when touch-up work is done or excess stain is not wiped off or otherwise removed.

**Dichroic Effects.** When a coloring agent has one hue when used in small percentages and a different hue in stronger percentages, this two-color concentration effect is known as dichroism. It is a far more prevalent phenomenon than is generally realized. The familiar "top-tone" and "under-tone" of pull-down tests are dichroic effects produced by viewing the color through films of different thicknesses. Other examples are obtained from many yellows, as reddish yellows may appear orange or red in concentrated applications. Similarly, some reds become pinks on dilution, whereas others yield oranges. Again, nearly all blues will transmit so much red light that, if applied in concentrated solutions in coatings, as on an electric light bulb or decorative transparent filter, the light may gleam red instead of blue, while by reflected light the coating may appear black. A final, specific example is amaranth (C.I. 184), which in a gelatin coating, or in solution, will change through very bluish red to scarlet to red-orange as the dye concentration is increased.

**Fluorescence.** Fluorescence is a special effect which many consider dichroic. It refers to the property of some agents, some colored, some visibly colorless, to transmute invisible ultraviolet radiations into visible color emanations. It is largely a reflectance phenomenon. Probably the best-known example is uranin (C.I. 766), which in solution, or in films, will appear as a canary to reddish yellow by transmitted light, and as a very yellowish green by reflected light. In the dark this dye appears as a very greenish yellow to yellowish green when subjected to ultraviolet radiations (24).

**Reactive Conditions.** Many dyestuffs are  $pH$  indicators as they change in hue with changes in acidity or alkalinity. Such changes are often the cause of non-uniform color effects. For example, many wood stainers have been troubled by having an oak or walnut stain change in a day or two to a reddish brown. This change has been traced in some cases to a change in the  $pH$  of the wood surface. For example, the surface of wood may slowly become acid, either from natural acids drawn by evaporating moisture from the interior or from residual "clearing" acid, such as oxalic acid, used in preparing the wood. If to this acid surface a stain is applied containing dyes sensitive to acid [as in the case of an oil stain containing Oil Yellow (C.I. 19), which goes red with acids], spotted or unevenly blotched redder brown areas will be formed slowly. Even the use of resins high in acid number in stains may cause color changes. Exposure to acid fumes, washing with alkaline reagents, contact with perspiration and other body liquids, metallic salts, and a wide miscellany of residual industrial processing agents or casual materials may affect greatly the permanence and appearance of a stain.

**Penetration, Sublimation, Efflorescence, Rubbing.** Applied coloring matters do not always stay where they are first applied. They may sink or penetrate into the interior, effloresce from pores or films, or sublime or rub off from the surface. These tendencies vary greatly almost with every application.

**Cleanliness, Surface "Wettability."** Stain applications are affected by the surface tension of the solid-stain interfaces. Usually a soiled, oily, wet, waxy, or dusty condition will promote uneven color effects. Under the best conditions, many natural materials contain water-repellent resins, waxes, and oils, and, unless removed or their effect counteracted by using wetting agents, aqueous stains and often stains in other vehicles will not uniformly color the surface.

### Judging Color Effects

All the factors just discussed also affect the judging of color. In Table II are listed some of the many other factors that influence color comparisons. These are as varied and insidious as partial color-blindness, light sources, hygroscopic condition, and psychological bias (30).

### Terminology Used by Colorists

When making color comparisons and using psychological terms, colorists compare the hue, brightness or purity, and saturation or tinctorial strength. To compare brightness, one color is called "brighter"



TABLE II

## SOME FACTORS INFLUENCING THE JUDGMENT OF COLOR

1. Color aptitude	Color-blindness is a handicap
2. Light sources	Use standardized light
3. Location of studies	Upper floors better than the cellar
4. Light intensity	Sunny days better than cloudy
5. Eye strain	Color memory, fatigue
6. Multicolor effects	Viewing colors in juxtaposition
7. Dichroism	Under-tones, and top-tones
8. Transparency	Also gloss, and matte effects
9. Bronze	Iridescence, fluorescence
10. Reaction effects	pH changes, fumes
11. Photolysis	Photochemical changes
12. Condition	Wet, moist, or dry
13. Latent solubility	Graining-out
14. Penetration	Uneven absorption
15. Cleanliness	Finger marks, grime

or "duller" than the other. Saturation may be compared as "lighter," "darker," or as strength may be "weaker" or "stronger." The hues are called red, orange, yellow, green, blue, purple, brown, and black, or in the adjective form as reddish, orange, yellowish, greenish, bluish, purplish, and brownish (26). Intermediate hues are indicated by combined hue terms, such as red-yellows and blue-greens, for example. At present, in general practice, two reds may be compared for hue as being yellower or bluer, and, similarly:

Reds are compared as being yellower or bluer.

Oranges are compared as being redder or yellower.

Yellows are compared as being redder or greener.

Greens are compared as being yellower or bluer.

Blues are compared as being greener or redder.

Purples are compared as being bluer or redder.

To describe one blue as being bluer than another is meaningless but to say one is redder, brighter, and more saturated (stronger) adequately orients it versus the other for comparison purposes.

**Exact Color Specification.** A serious effort is being made by some physicists and colorists to define exactly the chromaticity values of specific hues (21, 26). Standard shade cards (18a, 22, 32, 35, 37) and a color dictionary are also available. Most manufacturers of stains also issue hue or "shade" cards, but these are far from being standardized, as comparisons of exhibits from different sources readily disclose. Particularly the wood colors, such as red mahogany, brown

mahogany, cedar, cherry, walnut, oak, and maple, rarely match in color obtained from different manufacturers, or in successive editions from the same manufacturer. Maerz and Paul (22) have tried to indicate the shade corresponding to many popular color names as determined by the consensus of trade opinion. Of course, not all their colors are accepted by some stainers. In general, however, the color plates listed in Table VIII have been found useful and practical standards for the principal wood colors. The student should note the fact that the popular wood color name may refer to a conventionalized hue, one often none too closely related to the actual color of the natural wood of that name.

### THE MECHANISM OF STAINING

There is no general agreement among investigators on the exact mechanisms of staining. Undoubtedly, the fixation of coloring agents is the result of different forces in differing applications, and is influenced also by chemical natures and physical properties of the dye-stuffs and pigments. Actual chemical combination with surface materials may occur, and probably does occur between some dyestuffs and mordants for them previously applied. In other cases, the coloring effect may be due to deposition (adsorption), mechanical admixture or entrapment, or to the less understood forces of dipole attraction and absorption. In stains containing resinous or amphoteric protein binders (such as casein or glue) there may be reactions between the dye and the binder. If the dye or pigment is inert, the binder may just hold the coloring agent glued, as it were, to the surface to be colored.

### THE GENERAL APPLICATION PROPERTIES OF SYNTHETIC DYES

By far the greater volume of modern stains contain soluble synthetic dyes as the coloring agents. Professional colorists have found it a great aid to classify these dyes broadly in accordance with their application properties as well as into their chemical groups. Accordingly, for ready reference many of these general properties are tabulated in Table III and are further discussed in the text. These groups are based on the affinities of dyes for materials of animal, vegetable, mineral, or synthetic origin, and/or their behavior under acid, neutral, or basic conditions, or their major solubility characteristics.

TABLE

Application Group	General Nature	Major Affinities	Hues	Brightness
Acid Dyes	sodium salts of color acids	notes 1, 5	full range	v. good
Acid-Mordant Dyes	acid dyes that react with mordants	notes 1, 5, 2	full range	moderate to good
Basic Dyes	salts of color bases	notes 1, 3, 5 also clays	full range	v. bright
Direct Dyes	sodium salts of color acids	notes 3, 4, 5	full range	moderate
Develop Dyes	direct dyes that can be diazotized and developed	notes 3, 4, 5	full range	moderate
Naphthosol Dyes	naphthosols-diazo amines, formed on material	note 6	full range	good
Oil-Soluble Dyes— Group 1	water-insoluble azo dyes	note 6	note 10	good
Group 2	water-insoluble anthraquinone dyes	note 6	note 11	moderate
Group 3	fatty acid salts of basic dye bases	note 6	full range	v. good
Group 4	fatty acid salts of azine dye bases	note 6	note 13	good
Group 5	varnish dispersions of rosaniline blues	note 6	blues only	good
Spirit-Soluble Dyes— Group 1	amino condensation products	note 6	full range	moderate
Group 2	basic dye bases	note 6	full range	v. bright
Group 3	basic dye-mordant mixtures	note 6	full range	good
Group 4	azine dye bases and hydrochlorides	note 6	note 13	good
Group 5	acid dye-basic dye complexes	note 6	full range	good
Sulfur Dyes	organic polysulfides	notes 7, 6	note 12	moderate
Vat Dyes	complex indigoid and anthracene derivatives	notes 8, 6	full range	moderate to good

1. Have direct affinity for proteins.
2. React with acidic metallic mordants.
3. Color cellulosic material high in tannin.
4. Have direct affinity for cellulosic matter.
5. Have direct affinity for amphoteric matter.
6. Colors by dissolving into, absorption, or deposition.
7. Directly dye cellulosic matter from  $\text{Na}_2\text{S}$  solutions.
8. Directly for cellulosic and amphoteric matter from alkaline reducing solutions.
9. Fastness varies widely from poor to excellent.
10. Only red, scarlet, orange, yellow and black colors are available.
11. Only red, green, blue, and purple colors available.
12. Full range of hues, except bright reds.
13. Black and navy blues available.
14. Soluble in aqueous sodium sulfide solutions.
15. Soluble in alkaline, reducing vats.

## III

Tinting Power	Solubility	Fastness			
		Light	Heat	Bleeding	Rubbing
v. good	SW Gly, Gly Et Insol Ar-H, Ac-H	good	good note 9	sparingly in Alc; note 9	moderate to good
good	same as acid dyes	good on mordants	good note 9	sparingly in Alc; note 9	moderate to good
v. powerful	SW Alc, Gly, Gly Et	fugitive	note 9, some ex.	badly in Alc	poor
good	SW Alc, Gly	moderate	note 9 good	sparingly in Alc	moderate
good	SW Alc, Gly	moderate to good	note 9 good	sparingly in Alc	moderate
good	Insol W SS Alc	good	note 9 good	bleed in Alc	moderate
v. good	S Ar-H, Ac-H, Rs; some are soluble in Alc, oils, and waxes	moderate	good	badly in hydrocarbons and Alc	moderate to poor
moderate	S Ar-H, Ac-H, Rs, oils	good	moderate note 9	badly in hydrocarbons	moderate
moderate	S Alc, Ar-H, OV	fugitive	moderate note 9	badly in Ar-H, Alc, Gly Et	moderate to poor
good	S Ar-H	good	good	badly in Ar-H, Alc, Gly Et	moderate to poor
good	Dye SS Alc	moderate	moderate	badly in Alc	moderate
moderate	S Alc, Gly Et	good	moderate	badly in Alc	moderate
v. powerful	S Alc, Ar-H, Gly Et, Kt	fugitive	note 9, some ex.	badly in Alc, Ar-H	poor
moderate	S Alc, or W-Alc mixtures	moderate	moderate	badly in Alc	moderate
good	S Alc, Alc—Ar-H mixtures	good	good	badly in Alc	moderate
good	S Alc, Gly Et	moderate	moderate	badly in Alc	moderate
moderate	note 14	good	moderate	non-bleeding	moderate to good
moderate	note 15	excellent	good	sl. in Ar-H	moderate to good

*Abbreviations:*

Ac-H	—Aliphatic Hydrocarbons
Alc	—Alcohols
Ar-H	—Aromatic Hydrocarbons
ex.	—Excellent
Gly	—Glycols
Gly Et	—Glycol Ethers
Insol	—Insoluble
Kt	—Ketones
OV	—Vegetable Oils
Rs	—Resins
S	—Soluble
SS	—Sparingly Soluble
SW	—Soluble in Water
v.	—Very
W	—Water

### Acid Dyes

The "acid dyes" group is comprised of colored organic chemicals (dyes) from the nitro, azo, pyrazolone, quinoline, triphenylmethane, diphenylnaphthylmethane, azine, xanthone, and anthraquinone groups (5, 12, 19, 34, 38). The great majority of these are marketed as mono, di, or trisodium sulfonate derivatives of (usually) soluble color acids. Customarily they are applied in warm, weakly acidic dyebaths or solutions, inasmuch as under such conditions they possess direct affinity for amphoteric materials, proteins, and fibers of animal origin. Strangely enough, although having little direct affinity for cellulose, many of them are excellent wood stains. As a group they offer a full range of bright hues of good tinctorial power, and are reasonably resistant to light, heat, and acid reagents. Individually, however, they may vary widely in one or more respects—as to fastness, solubility, and degree of affinity. As customarily prepared, most of them contain Glauber's salt (calcined sodium sulfate) or sodium chloride, formed during processing or added as a standardizing agent. Accordingly, with the general exception of certain ink and pencil blues, violets, and eosin (tetrabromfluorescein), very few can be used in concentrated water solutions, owing to the "salting-out" action of the inorganic salts. Some of these dyes are soluble in alcohols, glycols, and glycol ethers. The acid colors are extensively used in water stains, decorative inks, artists' water colors and "brush out" pencils, and calender stains.

### Acid-Mordant Dyes

These are a special or subgroup of the acid dyes, and are characterized by having one or more hydroxy radicals in the molecules, the hydrogen of which is replaceable by metals. Therefore, they are "adjective" in nature, possessing affinity for metallic mordants. This reaction should not be confused with the substitution of the hydrogen of sulfonic acid by metals to form lakes, as discussed by Dr. Pratt, in Chapter 2 of Volume II. They are not frequently used as stains. Soxhlet cites an interesting study of results obtained with a soluble form of alizarin (dihydroxyanthraquinone, a hydroxy ketone), which, together with a check-run on birch, is tabulated in Table IV. These dyes can be used as acid dyes, but usually change in hue, brightness, saturation, and fastness properties when combined with metallic mordants (7).

TABLE IV

STAINING (WOOD) OVER METALLIC MORDANTS WITH AN ACID-MORDANT DYE

Mordanting Solution	On Pine, Elm, and Maple *	On Oak †	On Birch †
Alum, 3%	deep red	blood-red	bri. red-orange
Barium Chloride, 1%	brown	brown	lt. orange-brown
Bismuth Nitrate, 1.5% plus Nitric Acid	red brown	dark nut-brown	red-orange ‡
Cadmium Chloride, 2.5%	reddish coffee-brown	coffee-brown	red-mahogany
Calcium Chloride, 1%	burnt sienna-brown	red-brown	red-mahogany
Chromium Fluoride, 3%	red-violet	Havana-brown	med. red-brown
Cobaltous Sulfate, 2.5%	lilac to amethyst	dark walnut	v. bluish red
Cupric Sulfate, 2%	red-violet to cherry	brown-violet	maroon
Ferric Chloride, 1.6%	dark yellow-brown to yellow-black	yellowish-blk.	rosewood
Ferric Sulfate, 2%	red-black	black	brownish-black
Lead Acetate, 3.5%	red-violet	bordeaux-violet	bordeaux
Magnesium Chloride, 2%	dark brown	dark brown	v. bluish-red
Manganous Sulfate 2.5%	red violet-brown	walnut brown	v. bluish-red
Nickel Sulfate, 2.5%	lilac	dark red-brown	dark red-purple
Stannous Chloride, 2%	Pernambuco red to brown	red-brown	orange ‡
Sublimate Crystals, 2.9%	red-brown	coffee-brown	yellow-brown
Tartar Emetic, 2%	orange-red to dark brown	coffee-brown	red-orange ‡
Zinc Sulfate, 2.5%	dark cherry-red	dark red-brown	v. bluish-red

\* Tabulated from data cited by Soxhlet (15, 36).

† Using a 2% aqueous solution of alizarine red S (Colour Index 1034).

‡ After-treated with ammonia.

## Basic Dyes

These are usually the hydrochlorides, oxalates, or zinc chloride double salts of color bases of the azo, azine, xanthene, oxazine, thiozine, ketonimine, acridine, triphenylmethane, and diphenyl-naphthylmethane groups of dyes. They lack the sulfonic acid radicals of their otherwise chemically similar acid dye counterparts. In most cases their sparingly soluble dye bases are precipitated by adding alkalis to solutions of their salts. These dyes are incompatible in water with many acid and direct dyes as they tend mutually to precipitate each other. The reactive tendencies of a basic dye as compared to an acid dye can be better appreciated if it is remembered that a basic dye nucleus is a positive anion, much like the metal element of an hydrox-

ide, whereas an acid dye nucleus is a cation, comparable to the negative element or radical of an acid. Consequently, the reaction of basic dyes with acidic mordants is similar to that of basic hydroxides with acidic salts.

The mordants most commonly used for basic dyes are tannic acid, gallic acid, oak galls, sumac, and other vegetable tannins and tanning agents. Frequently cellulosic materials, such as wood, cloth, straw, and paper board, if lacking sufficient natural tannins, are treated with hot tannin solutions, and the mordant set by a second treatment with metallic salts, such as potassium antimony tartrate (tartar emetic) or ferric chloride.

Their bases and fatty acid dispersions will color many vegetable and animal oils. Many of their salts, as well as their bases, are soluble in alcohols, glycols, and glycol ethers and in these liquids they comprise one group of the spirit stains. Their concentrated solutions are the basis of many of the highly important so-called aniline inks. These dyes rarely contain appreciable amounts of inorganic salts, as they are usually standardized with non-polar materials, for which purpose dextrin is the most commonly used product. Accordingly, concentrated aqueous solutions of them can be prepared.

This group, as a class, are the most beautiful, bright, and tinctorially powerful of all known coloring agents. Unfortunately, they are relatively fugitive to light. They are widely used, being almost universal stains. They tend to color nearly all natural products to some degree and a great many synthetic materials. Many clays absorb them to approximately 2 per cent, which percentage can be increased by using tannins with them. They color proteins and other amphoteric materials and, accordingly, can be used with casein, albumin, or gelatin binders to stain materials for which they have little affinity. Some of their salts and bases have a marked effect on the rate of polymerization of some resins, generally accelerating the process, although some derivatives may retard the reaction.

### Direct Dyes

The name of this group of dyes is derived from their property of substantivity or direct affinity for vegetable (cellulose) and many amphoteric materials. These dyes are chemically in the azo, stilbene, and thiazole groups, most of them being sodium sulfonates. As a group they are precipitated by acids (having generally insoluble color acids) and by heavy metal salts (as in hard water). Accordingly, they are usually used in neutral or alkaline media. Their hues are

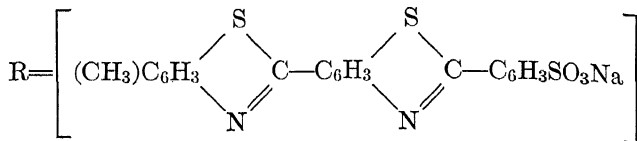
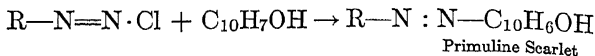
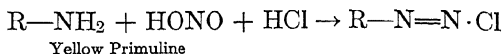
relatively soft in tone, rather than brilliant. As their molecules are massive, they are usually tinctorially weaker than the acid dyes. Moreover, their fastness to light and reagents is generally inferior and their hues less brilliant. These features, coupled with their limited solubility, make them less useful than acid dyes in stains. Much of their limited solubility is due to the relatively large percentage of common salt customarily left in them during manufacture. Because of their direct affinity for cellulose, they are sometimes used as stains for wood, grass, jute, canvas-covered surfaces, and paper (25).

### Develop Dyes

These are a special grouping of some direct dyes that can be further processed after application by diazotizing and coupling ("developing") with selected phenols, naphthols, and amines. Their principal advantage as stains is for producing stencil effects by the "diazotype" processes. Briefly, this process consists of staining a surface with one of these dyes and then producing the diazo derivative by a treatment with dilute nitrous acid (sodium nitrite plus hydrochloric or sulfuric acid). These diazo compounds are decomposed by exposure to light for varying periods. Accordingly, stencils or photographic negatives can be used as masks and the photolysis thereby restricted to designated areas. After exposure, the stain can be treated with  $\beta$ -naphthol solution or other developer, which will react to complete the formation of a new color of different hue, brightness, and saturation with the undecomposed diazo complex. The result is a two-color design or print.

The after-treated develop dyes are somewhat faster to light and reagents than many of the direct dyes, but otherwise their affinities and properties are very similar.

A typical yellow develop dye is primuline (C.I. 812), and its reactions on diazotizing and developing with  $\beta$ -naphthol to yield a scarlet are shown below:





### Naphthosol Dyes

The naphthosol dyes are sometimes called "ice colors" or "ingrain" colors because they are produced by combining stabilized diazotized aromatic amines with naphthols or oxynaphthoic acid derivatives. These dyes are useful as lakes. Their chemistry has been discussed by Dr. Pratt in Chapter 2 of Volume II.

However, it is possible to produce these dyes directly on the surface of materials. This may be done by applying the naphthol or other coupling agent first, drying, then after-treating with a diazotized amine solution. Theoretically the process can be reversed by first applying the diazotized amine and following with the naphthol solution; but experience has shown the first procedure usually gives better control of results.

The simpler azo dyes can also be formed directly on the material by a similar method. For example, a surface impregnated with a solution of  $\beta$ -naphthol in caustic soda can be treated with a solution of diazotized paranitraniline, upon which para red is formed directly on the material. If the diazotized solution be applied through stencils, design effects can be produced.

### Oil-Soluble Dyes

There are five major groups of these dyes. They are characterized by being insoluble in water, and soluble in hydrocarbons or mixtures of aromatic hydrocarbons and alcohols. Some are insoluble dye molecules very similar to the acid dyes, but lacking salt-forming (hydroxyl or acid) radicals. Others are esters, salts or dispersions of basic dye bases and azine bases in fatty acids. They are widely used in stains.

**Group 1. Water-Insoluble Azo Dyes.** The insoluble azo dyes are a group of red, scarlet, orange, and yellow derivatives. They are closely related chemically to the acid dyes, being substantially the unsulfonated nuclei of those dyes. Having relatively small molecules, as dyes go, they are tinctorially powerful. Their hues are moderately bright. Their fastness properties vary widely, not only in comparison with one another but also because they are greatly influenced by the media in which they are used. For example, many of them are quite fugitive in most nitrocellulose lacquers, fading badly during two to ten hours of exposure to sunlight, whereas the same dyes may stand as much as a hundred hours of exposure in a polystyrene or methacrylate coating. It is difficult to predict by analogy their probable resistance in one medium from their fastness in another; a dye that

might be fast enough to use in castor oil might be much more fugitive in a cottonseed oil application.

These dyes are soluble or dispersible in both aromatic (toluol) and aliphatic hydrocarbons (petroleum), although to a much lesser degree in the latter type. They dissolve or disperse in animal, mineral, and vegetable oils, greases, and waxes, and in most of the hydrocarbon soluble resins. They are insoluble in water but can be used in water in oil emulsions. They are soluble in aliphatic esters, the chlorinated aliphatics, chlorinated naphthalenes, chlorinated diphenyls, chloroform, and carbon tetrachloride. Accordingly, they are used extensively in oil stains, lacquer stains, varnish stains, and rubber solutions. A few are soluble in alcohols and ketones, but in general they are seldom used primarily in these liquids.

One feature of these dyes that is of great practical importance to the stainer, particularly when varnish stains are used, is their anti-oxidant effects. Customarily 1 to 4 per cent solutions of these dyes in varnishes are used as varnish stains on wood, and at these concentrations the dyes largely nullify the catalytic effect of the metallic soap driers. As a consequence, the drying of a varnish containing them may be retarded greatly, sometimes for periods as long as several days.

**Group 2. Water-Insoluble Anthraquinone Dyes.** These constitute a group of green, blue, violet, and a few red dyes that fortunately supply the spectrum colors (blue-end) missing in the group of water-insoluble azo dyes. In general, these dyes are less soluble and somewhat faster to light and reagents but, otherwise, they closely approach the general properties of the water-insoluble azo group. When solutions of these dyes alone are applied they deposit as dull, grayish, and tinctorially weak stains. To get their true color effects they have to be used with a film-forming or coating agent.

For some reason, at present obscure, most of these anthraquinone dyes will decolorize, or go grayish in storage (even in the dark) when used in certain waxes, particularly in certain crayons or candles. Consequently, they should be used with caution in polishing stains.

**Group 3. Fatty Acid Esters of Basic Dye Bases.** The basic dye bases can be dispersed in fatty acids to produce products soluble in some animal and vegetable oils. Occasionally, if made as pastes or liquids by using unsaturated acids, such as oleic or linoleic acids, some of the mineral oil fractions are miscible with them, at least temporarily. These derivatives are useful as a means of introducing the

brilliant basic dyes into oleoresinous and waxy media, and are much used as toners in inks.

**Group 4. Fatty Acid Dispersions of Azine Bases.** The synthetic dye "oil blacks" are usually dispersions of nigrosine bases and induline bases in stearic acid (solids) or oleic acid (pastes and liquids). These are soluble in aromatic hydrocarbons, and in this form are used in large quantities in oleoresinous and waxy stains and polishes. As full, strong colors they have good fastness to light and reagents, but as grays or toning colors they are less fast. They yield bright, attractive gloss blacks. In oleoresinous varnishes they have a decided anti-oxidant effect.

**Group 5. Varnish Dispersions of Rosaniline Blues.** The color acids of some rosaniline blues (C.I. 704, 707) are insoluble in water but can be dispersed into varnishes and other resinous vehicles. These so-called alkali blue toners are used in large quantities for shading black printing inks. Sometimes they are used in combination with the phosphotungstate or phosphomolybdate derivatives of basic dyes for this purpose. Their hues are bright and tinctorially powerful, often bronzy. They have good resistance to dilute acids and moderate resistance to alkalies and light. They are insoluble in hydrocarbons, but the dye bleeds into alcohols. Their use is indicated when it is not desired to have the coloring agent penetrate into or through a surface as deeply or readily as the vehicle.

### Spirit-Soluble Dyes

There are several dyestuffs in the acid, acid-mordant, direct, and oil-soluble dye groups that are sufficiently soluble in alcohols to be useful occasionally in spirit and lacquer stains. The various patent blues (C.I. 712, 714), eosine (C.I. 768), and methanil yellow (C.I. 138), direct black (C.I. 581), and oil yellow T (C.I. 17) are representative of them. In addition, however, to these miscellaneous selections, there are five major groups of dyestuffs usually classified by the trade as the spirit-soluble dyes: (a) amino condensation derivatives of metallized azo and other acid and direct dyes; (b) the basic dye bases; (c) proprietary mixtures of basic dyes with spirit-soluble mordants or laking chemicals; (d) nigrosine and induline (azine) salts and bases; (e) spirit-soluble acid dye-basic dye complexes, and proprietary mixtures of selected, self-precipitating acid dye-basic dye mixtures. Dyes from each of these groups are widely used in stains.

**Group 1. Amino Condensations of Metallized Azo and Acid Dyes.** There are several distinctive types of products within this classifica-

tion. Most of them are covered by current patents as to manufacture and uses. Paranitraniline-azo dye (40) and guanidine-azo dye (40) complexes are two other series of these dyes. These products are sparingly soluble in water. They are soluble in alcohols and glycol ethers and through these media are incorporated into many lacquer stains, spirit stains, and non-grain-raising wood stains. In general, they do not tolerate large percentages of hydrocarbons in solvent mixtures, nor are they always completely compatible with certain resins, notably unrefined shellacs. Their hues are reasonably bright, their tinctorial power is moderate to good, and their resistance to light is moderate to excellent. Although rather high in price, their use is indicated in quality work.

**Group 2. Basic Dye Bases.** The dye bases of the basic dyes are useful spirit-soluble stains. They are sparingly soluble in water, particularly alkaline water, but dissolve readily in acids to yield dye salts. They are somewhat soluble in aromatic hydrocarbons to yield almost colorless or weak, red-brown colored solutions, and it is sometimes startling to see objects, when dipped into such weakly colored liquids, become stained to strong and brilliant hues. These solutions are particularly useful for staining waxy, oily, or dusty surfaces, as the vehicle penetrates through the grime. In contrast, the alcoholic solutions of these dyes are strongly colored. In alcoholic vehicles these dyes may be added to spirit stains and lacquers. Their use is particularly indicated when it is inadvisable to have present the hydrochloride or other acid salt of the basic dye, as is sometimes the case for electrical or chemical reasons.

**Group 3. Basic Dye-Mordant Mixtures.** These proprietary mixtures consist largely of basic dyes and spirit-soluble precipitating chemicals. Louis N. Sahm first patented (33) such mixtures of basic dyes and tannic acid in 1912, having developed them as a means of staining hat straw with a dye that would not run or bleed during a rain. These complexes enable stainers to use the beauty of the basic dyes and still obtain results fast to water and moderately fast to light economically. They have been used in large volume for years as stains for wooden fruit crates, baskets, and paper-board containers, on leather, on various materials for stencil inks, and as the basis of many of the so-called aniline, high-speed printing inks. They are compatible with shellac and most of the alcohol-soluble resins, but are not recommended for general use in lacquer stains because of their acidity.

**Group 4. Azine Dyes.** The spirit-soluble nigrosines and indulines are probably used in larger volume than most other staining agents.

These azine dyes yield navy blue to jet black shades, bright and strong tinctorially. They are moderately to very soluble in alcohol, sparingly soluble in aromatic hydrocarbons, and highly soluble in mixtures of aromatic hydrocarbons and alcohols. Almost all their freshly prepared solutions, at concentrations of 1 per cent or higher, contain some seemingly less soluble fractions that are preferably removed before using by centrifugal separation, by filtering or being allowed to settle. Generally, they are not compatible with the spirit-soluble amino condensation dyes in Group 1. These dyes yield "bloomy" full blacks in the proper media, and as blacks have very good fastness to light. Used in weak percentages they yield grays that have only moderate resistance to light. They are the basis of most of the gloss-black lacquer stains and insulating spirit varnishes and are used as leather stains (3), wood stains, and in marking and stenciling inks.

**Group 5. Acid Dye-Basic Dye Complexes.** These are balanced proprietary mixtures or previously co-precipitated complexes of acid and basic dyes. Usually, the constituent dyes, as well as their precipitated product, are soluble in alcohols. These mixtures have much of the beauty of the basic dyes, with some gain in fastness to light from the presence of the acid dye. Moreover, a well-balanced mixture has good resistance to water. They are used chiefly in aniline printing inks and lacquer stains.

### Sulfur Dyes

These are a group of polysulfide dyes. They are only sparingly soluble in water, but are readily soluble in water containing 10 per cent of sodium sulfide or other soluble sulfides. From these solutions they have direct affinity for cellulosic matter, particularly when applied nearly at boiling temperature. The hues available do not include bright reds. Generally their hues are but moderately bright, and their tinctorial strength is also moderate. Being polysulfides, some of them show some tendency to develop acids. These stains are resistant to water and light, and show very little tendency to bleed into varnish or lacquer top coatings. They are not used frequently, but give excellent results in the hands of experienced stainers.

### Vat Dyes

The name vat dyes probably derives from the ancient dung vats used for indigo dyeing. This group is comprised of the water insoluble, chemically complex, hydroxyketone, hydroxyquinoline, and hydroxylactone derivatives of naphthaline and anthracene, including amino,

imide, azine, acridine, and other derivatives of anthraquinone. The production of some of these dyes synthetically is considered among the finest achievements of modern chemistry. These dyes are insoluble in water, sparingly soluble in hydrocarbons and alcohols, soluble in concentrated sulfuric acid, and are re-precipitated from the latter solvent on dilution with water. Their leuco compounds are soluble in water, and it is in this form that they are generally applied. These solutions are prepared by warming the vat dye at 120° F. to 180° F. for 20 minutes in water containing approximately 5 per cent of caustic soda and enough sodium hydrosulfite to produce the leuco compound. The proportions of each reagent and the temperature have to be adjusted for each dye for best results, and usually the recommendations of the manufacturers should be ascertained.

The leuco compounds show substantivity for cellulosic and some amphoteric materials. On drying their solutions, the original vat dye is reformed by oxidation. Their hues are reasonably bright, but their tinctorial value is moderate. As a group they are about the most resistant of any to light and reagents, although they vary greatly in these properties individually. Their hues and fastness results are also affected by the method of application and other local conditions. Being necessarily high in cost, they are used less frequently than other stains.

The vat dye powders themselves are used on occasion as organic pigments in some suspensions with binding agents.

#### VEHICLES FOR STAINS

Both the ancient and modern stainers have used water, oleoresinous oils, solutions of ferments (alcohol-ester mixtures), alcohol, and turpentine as vehicles for stains. The modern stainer, however, has a list of more than 208 solvents and approximately 100 plasticizers (31) from which to choose in formulating stain vehicles. Moreover, there are now available many new binding or coating materials, particularly new synthetic resins and oil fractions. The possible mixtures of these binders and liquids are almost endless in number. As varnishes, lacquers, enamels, inks, and crayons they are used as vehicles for coloring agents for staining.

#### STAIN FORMULATIONS

With approximately 1,000 synthetic dyes (1, 6) and literally thousands of their mixtures on the market, the theoretical possible coloring

## TABLE V

## REPRESENTATIVE STAIN FORMULAS

(Note: In all these formulas dyes of the same group can usually be substituted for those listed.)

*Orange Acid Color Stain*

Orange II (C.I. 151).....	2½ oz.
Mucilage.....	10 oz.
Water.....	1 gal.

*Red Direct Color Stain*

Benzopurpurine 4BX (C.I. 448)	2½ oz.
Methylcellulose *.....	2½ oz.
Water.....	1 gal.

\* Rosin size can also be used.

*Black Sulfur Color Stain*

Sulfur Black (C.I. 978).....	12 oz.
Sodium Sulfide Conc.....	36 oz.
Soda Ash.....	6 oz.
Water.....	64 oz.

*Blue Vat Dye Stain*

Vat Blue BLD Dbl. Pdr. (C.I. 1114).....	2 oz.
Sodium hydrosulfite.....	1½ oz.
Caustic Soda (30° Be).....	4 oz.
Water at 50° C.....	1 gal.

Boil and dilute with water to 1 gal.  
After application, rinse well with water.

After application, rinse well with warm  
soapy water.

*Blue "Aniline" Ink Stain*

Dybyrte Blue N-4338B.....	12½ oz.
Refined Shellac (5-lb. cut).....	1 qt.
Alcohol.....	3 qt.

*Blue Pigmented Wall Stain*

Ultramarine Blue †.....	100 lb.
Casein Paste ‡ or Rosin Size...	11 gal.
Thin with water as needed	

Dissolve the dye in the alcohol, and then add the shellac solution. This formula can be used for all spirit-soluble dyes that are soluble enough.

† Use a water-dispersible type.

‡ Casein.....	18 lb.
Borax.....	2½ lb.
Ammonia.....	½ lb.
Water at 110° F.....	12½ gal.

Note: Addition of 1 qt. of formaldehyde just before using gives faster to water effects.

*Red "Brush-out" Lead Pencil*

Eosine (C.I. 768).....	40 parts
Calcium Stearate.....	15 parts
China Clay.....	37½ parts
Gum Tragacanth.....	7½ parts

*Red Stencil Crayon*

Rhodamine B Stearate.....	2 lb.
Calcophen Red Y.....	2 lb.
Stearic Acid.....	40 lb.
Beeswax.....	10 lb.
Paraffin.....	31 lb.
Carnauba.....	15 lb.

Make a 6% paste of the gum, and knead in the other ingredients. Roll and extrude. Dry at 90° relative humidity for six weeks. These leads are a solid form of artists' water colors.

TABLE V—*Continued**Orange End-Grain Sealing Stain*

Resorcline Brown Y (C.I. 234) . . .	1/2 oz.
Shellac-Borax Sol. § . . . . .	1 qt.
Water . . . . .	3 qt.

§ Orange shellac . . . . .	1 lb.
Borax . . . . .	4 oz.
Water . . . . .	1 1/2 gal.

Boil and dilute to 1 gal. Let settle, decant or filter, before bottling.

*Fast Gold Lacquer Stain*

Fast Spirit Yellow 2R Conc. . .	0.7 oz.
Fast Spirit Orange R Conc. . .	0.1 oz.
Fast Spirit Brown G. . . . .	0.2 oz.
Methanol . . . . .	3 1/2 qt.
Butyl Acetate . . . . .	1 pt.
Lacquer Base ¶ . . . . .	1 gal.
	2 gal.

¶ Use a nitrocellulose lacquer formulated to tolerate large percentages of alcohols.

*Black Stencil Ink or Varnish Stain*

Carbon Black . . . . .	25 lb.
Alkali Blue Toner . . . . .	10 lb.
Lithographic Varnish . . . . .	49 lb.
Cobalt Drier . . . . .	6 lb.
Paste Drier . . . . .	10 lb.

*Violet Paper-Board Stain ¶*

Dybryte Violet X . . . . .	2 1/2 oz.
Alcohol . . . . .	1 1/2 qt.
Water . . . . .	2 1/2 qt.
	1 gal.

¶ This type of stain will color almost all materials, much used for fruit crates, baskets, etc.

*Blue Black Gloss Spirit Varnish*

Nigrosine SSB (C.I. 864) . . . . .	5 oz.
Methanol . . . . .	2 qt.
Shellac (5 lb./cut) . . . . .	2 qt.

*Black Marking Stain or Ink*

Nigrosine Base (C.I. 864) . . . . .	12 oz.
Cresylic Acid . . . . .	3 qt.
Phenol . . . . .	1 qt.

Let settle or centrifuge to clarify.

1 gal.

*Non-Bronzy Black Stain*

Direct Black 200% (C.I. 581) . . . . .	20 oz.
Acid Blue Black Ex. Conc. (C.I. 246) . .	18 oz.
Direct Yellow Brn. K. Ex. (C.I. 596) . .	2 oz.
Water . . . . .	11 gal.
Resin Emulsion (Aerotex 140) . . . . .	1 1/2 gal.

formulations are almost innumerable. Each dye and compatible dye mixture can be used as stain colors with varying advantage. The choice of dye to use is governed by such factors as hue, solubility, compatibility, fastness specifications, availability of dye and technical service, process engineering requirements, and cost. Handicraft shops and small volume users preferably should use proprietary stains, as seldom have they the technical aid and the research and production facilities for the satisfactory and economical manufacture of stains.



However, for the guidance of experimenters and technicians there are found in Table V some of the more commonly used formulas for wood stains, varnish and lacquer stains, and inks. These formulas can be modified or used as given on a wide range of materials.

### APPLICATION METHODS

Early craftsmen applied stains usually by brushing or by swabbing on liquid or paste stains or by smoking or fuming (15, 36). Much of our present-day staining is done in a similar manner, often with the aid of machines.

To meet the speed-up needs of modern industry, stains are now frequently applied by passing (sheet stock) materials over rollers that transfer the stain from a color trough. These rollers can be plain (calenders) or engraved, or carry relief plates or type (printing machines). Completely fabricated objects can be dipped into staining baths, then dried and polished by tumbling in revolving drums containing sawdust.

Many familiar objects, such as picture frames, locks, hinges, hand-bag frames, and costume jewelry manufactured from lacquer-coated white metals (tin and aluminum), are colored to simulate bronze and gold by stacking them in baskets, dipping them in spirit stains, then promptly flushing them with water. In this process the lacquer coating is stained, not the metal. Local conditions govern the processing details.

Larger surfaces (floors, walls) and larger objects (furniture, machinery) are frequently stained by spray-gun and pressure or vacuum impregnation methods. These methods of application are often coupled with the use of force-drying (baking) procedures, together with the elimination of many sanding operations by employing stains formulated with non-grain raising (wood) liquids. Consequently production has been so speeded that it is not uncommon to have articles built, sanded, stained, coated, and shipped within the same day. Similar notable advances have been accomplished by using high-speed presses and calenders. Needless to say, these procedures have necessitated the development of stains uniquely suited to these remarkable applications.

### Health and Fire Hazards

There are certain precautions that instructors, students, handicraft and hobby shop operators, and in fact all stainers should take when

applying stains. Among them, safety and fire-prevention rank first in importance. Many stain vehicles are not only inflammable but toxic also (4, 17, 18, 23). Therefore, stains of unknown composition are advisedly assumed to be both hazardous to health and likely to form explosive mixtures. Consequently, they should be applied in well-ventilated places. It may be noted also that many of the United States of America have labor and fire laws forbidding the use of coal-tar benzene, aniline, nitrobenzene, carbon tetrachloride, 1,4-diethylene oxide, and similar toxic liquids in open systems.

### Unevenness of Applications

Generally, an excess of stain is applied when the stain is slow to dry and slow to penetrate, particularly in the use of water stains and oil stains on wood. After a few minutes the excess is wiped off. With quick-drying stains or when varnish and lacquer stains are applied, an excess is preferably avoided, in order to minimize streaking or the formation of pools on horizontal surfaces and runs or sags on vertical surfaces. If a stain is flowed onto an inclined surface, the lower portions will be much more heavily stained than the upper portions, and a longitudinal cross-section of the surface film would appear wedge-shaped because much thicker at the bottom of the plane. The end grain of wood frequently will appear darker than the side-surface grain colored with the same stain. This effect can be minimized by first sealing the end grain with a practically colorless film-forming solution, such as undyed resin solutions. Unevenness of appearance also may result by applying second coatings before the first is dry. Porous materials may absorb excess stain and later "sweat" it or exude it. A priming coat of undyed resin or size will help minimize this effect.

### Bleeding into Adjacent Coatings

Any coloring agent that is soluble or tends to bleed into certain liquids will naturally bleed into top coatings containing those liquids. This is extremely important when there are applied trim lines, transfer patterns, overprinting, and other designs for contrast or other multi-color effects. A white trim line applied over a nigrosine stain may dry gray (unevenly) as the black bleeds up into it. The stains can sometimes be "sealed" by applying an undyed film-forming solution over the stain. Shellac solutions are frequently used for this purpose.

TABLE VI  
SHADES OBTAINABLE BY RESTAINING COLORED OBJECTS

Original Self-Shade	Stain Applied	Color Effect Usually Produced
Red (Magenta)	Scarlet Orange Yellow Green Blue Purple	slightly yellower red sl. yellower, duller red sl. yellower, duller red dull maroons, blues, browns, blacks dull purples, maroons, browns, blacks v. bluish, brownish reds
Scarlet	Red Orange Yellow Green Blue Purple	sl. duller, bluer reds sl. yellower red sl. yellower reds to oranges reddish to greenish browns browns bluish reds
Orange	Red Scarlet Yellow Green Blue Purple	scarlets scarlets, red orange sl. effect, yellower orange dull olives, drabs browns, navy, blacks browns, blacks
Red-Yellow	Red Scarlet Orange Green Blue Purple	oranges to scarlet orange, scarlet orange bright olives, drabs dull greens, browns dull reds, browns, black
Green-Yellow	Red Scarlet Orange Green Blue Purple	dull oranges, scarlets orange, scarlet red-yellow, orange bright greens, olive sl. dull greens, yellow browns, drab dull reds, browns, black
Yellow-Green	Red Scarlet Orange Yellow Blue Purple	dull reds, browns, black olive, seal browns, drabs olives, to light drabs yellowish greens blue greens dull greens, browns
Blue-Green	Red Scarlet Orange Yellow Blue Purple	navy, browns browns, black olives, drabs yellow greens, light drabs sl. dull blues dull blues
Olive Green	Red Scarlet Orange Yellow Blue Purple	browns, black drabs olive green, light drabs olive green navy, dull greens dull navy, dull browns

TABLE VI—*Continued*

Original Self-Shade	Stain Applied	Color Effect Usually Produced
Sky Blue	Red Scarlet Orange Yellow Green Purple	dull purple, brown-reds brown-reds, browns dull greens, browns, black greens, light drabs blue green dull red-blues, dull blue purples
Red-Blue	Red Scarlet Orange Yellow Yellow-Green Blue-Green Purple	purples, brownish reds brownish reds, browns browns, blacks v. dull greens, drabs dull blue greens, light drabs sl. dull greenish blues blue purples
Purple	Red Scarlet Orange Yellow Green Blue	red purples brownish reds, browns v. dull reds, browns, blacks v. dull reds, browns, blacks dull blue purples, navy blue purple, red blues
Red Brown (Mahogany)	Red Scarlet Orange Yellow Green Blue Purple	v. dull reds, red brown v. dull reds, red brown red brown, yellow brown red brown, yellow brown browns, black browns, black duller browns, black
Green Brown (Drabs)	Red Scarlet Orange Yellow Green Blue Purple	red brown, black red brown, black yellow brown green brown v. dull greens dull navy, black red brown, black
Yellow Brown (Oak)	Red Scarlet Orange Yellow Green Blue Purple	red browns red browns dull oranges, yellow brown yellow brown dull greens, drabs drabs, blacks red browns, blacks
Black	All transparent stains give red, yellow, green, blue or violet tone blacks.	

*Notes:* 1. Color results vary with the relative tinctorial strengths of the original and the overstain. Pastel original or self-shades can be largely overpowered with strong topping stains, except by yellows and some oranges. Pastel or weak stains applied over strong self-shades have a minimum effect.

2. Grays may be considered as being tinctorially weak blacks.

### Optical Effects

Similar changes in hue may be purely an optical effect. For example, when a transparent blue is overprinted on a yellow, even though neither the blue bleeds into the yellow coating nor the yellow bleeds into the blue coating, the final color effect may be greenish. Again a transparent black applied over an opaque white may appear gray. (See Table VI.)

### "Blushing"

Vehicles that dry rapidly may chill the surface below the dew point, and the deposited moisture may "blush" the stain by disturbing the continuous jell structure of the film or binder. This blushing appears as white or light-refracting areas. The use of hydrocarbons in stain formulas may help to "blanket" the surface and, by thus keeping moist air from direct contact with it, help to prevent the formation of dew. Doing the work in a warm, dry atmosphere is probably the more practical precaution to take.

### Special Effects

Multiple-color effects can be obtained by applying stains through stencils and screens (screen printing) (13), by machine contour printing and engraving, by graining, spattering, stippling, and the use of transfers and crayons.

Stencils are used for artistic silhouettes and with marking inks on signs, show cards, containers, barrels, and a wide variety of surfaces. Screen printing is largely used on textiles, wall and floor coverings, leather cloth, and many other materials, and is usually used when high-quality repetitive decorative design work is necessary.

Graining is done by master varnishers by applying varnish stains in transparent films of uneven thickness over a light opaque ground color to simulate the grain effect of wood, and for this purpose special tools are used. For a more light-fast, but similar effect there is first applied a dispersion of insoluble pigments in drying oils (non-penetrating oil stains), using graining tools, or an artist's brush, and when this application has dried thoroughly an uncolored or colored transparent gloss varnish, lacquer, or other coating is applied.

Stippling is also an effect obtained by deliberately uneven film applications. An opaque ground color is applied and dried, then a second coating, colored to harmonize or contrast with the ground color. This second coating is formulated with a vehicle that is slow

to "pick up" or penetrate the ground coating and also not dry too quickly to permit stippling. The stippling is done either by rolling a special tool over the second coat or patting it with a crushed or crumpled sheet stock, generally a newspaper or cheesecloth. This treatment causes the second coat to dry in unevenly scattered areas and in films of various thicknesses, exposing more or less the ground coat color. Sometimes the decorative surface is not flat, but may be in relief, so that, by merely wiping much of the second application off again, the peaks or high spots will show the ground color, while the valleys or hollows will show the second coat.

Spattering is the process of applying a coarse spray (obtained either with a spray gun or by dragging a stick across a brush wet with the stain) as a second coating over a ground color. In this type of work a fast-drying vehicle is used to minimize any tendency for the scattered stain drops to spread, run, or streak. Spatter prints are obtained by masking portions of the ground color with removable stencils before applying the spatter coating. The silhouettes obtained when the stencils are removed can then be further decorated. Sometimes the spattering is done with several stains of differing color, but, unless done with a knowledge of color harmony and considerable physical skill, the effect may be none too attractive.

A skilled artist can apply stains with brushes to obtain a wide variety of color designs, pictures, and grain effects. As stains, they may use "water colors" which are solutions of acid dyes and water-soluble binders such as casein, glue, starches, gum arabic, alginates, locust bean, and other gums, or else pigment dispersions in these binder solutions. Oil stains, varnishes, lacquers, and enamels are also used. Spirit and non-grain-raising stains usually dry too quickly for most brush work, as brush marks are avoided only with great care when these stains are used.

### THE MAJOR TYPES OF WOOD STAINS

While antique and hobby shop craftsmen doubtless still make up numerous specialty stains, for large-scale production of stained wooden articles the trade has standardized four major types of stains: water-soluble, oil-soluble, spirit-soluble, and non-grain-raising. Typical practical color formulas for these stains are given in Tables IV, V, VII, VIII, IX, X, and XI, and many others can be found in the literature (2, 10, 11, 39). A discussion of these wood stains may be of general interest to all stainers.

### Water Stains

These are 1 to 3 per cent solutions ( $1\frac{1}{2}$  ounces to 4 ounces per gallon) of acid, acid-mordant, basic, direct, or develop dyes in water. Sometimes the use of a wetting agent, rosin-size or water-soluble binder, is advantageous, to improve penetration or to prepare the wood for top coats. The acid dyes are used for high-grade furniture and interior woodwork as they give the faster to light effects. Occasionally, for very fast results, solutions of leuco vat dyes are applied, in which case care is taken to wash off the residual chemicals. Basic dyes are used on short-lived objects, and where their brilliant hues add sales appeal, as on fruit crates and baskets. (There is one ancient water-soluble dye still used in large quantities as a basis for fast to light walnut shades. It is sap brown, and is prepared from peat or humus.)

In general, the use of water stains produces transparent effects that accentuate the wood grain. These stains have little tendency to bleed into oily top coats, or into lacquers formulated with a minimum of alcohols and glycol ethers present. They are economically important because of their good resistance to light, low cost, and the cheapness of their vehicle, water. (See Tables IV, V, VII, X.)

TABLE VII  
WATER STAINS FOR WOOD

	Colour Index Number	Red Ma- hogany	Brown Ma- hogany	Rose- wood	Cherry	Cedar	Wal- nut	Wal- nut	Oak	Golden Oak	Maple
Azo Rubine	179	40		55							
Crocein Scar- let MOO	252		15		4						1
Orange II	151	55	45	30	15	75	15	60	15	5	10
Metanil Yel- low Conc.	138		15		79			10	75	90	87
Nigrosine WSB	865	5	25	15	2	25	5	30	10	5	2
Sap Brown							80				
Approximate Ounces per Gallon		$2\frac{1}{2}$	2	2	$2\frac{1}{2}$	2	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	1	$2\frac{1}{2}$

### Oil Stains

There are two types of oil stains, the penetrating and the non-penetrating. Penetrating oil stains are essentially 1 to 3 per cent solutions of oil-soluble dyes in aromatic hydrocarbons (toluol, coal-tar naphtha) containing 5 to 10 per cent of resins, drying oils, or varnish. Part or all of the aromatic hydrocarbon can be replaced with the aliphatic types (petroleum fractions) for those formulations that contain the Group 1 and 2 oil-soluble dyes. The hues obtained are bright and transparent, and penetration is good. However, if too much drying oil is used, the oil will dry very slowly because of the anti-oxidant effect of the dyes. Again, a sealing coat is required to prevent or minimize bleeding into top coats of varnish or lacquer.

The non-penetrating oil stains are dispersions of insoluble pigments in dilute varnishes or drying oils. They are usually opaque or at best but translucent. Accordingly, they are used only when non-bleeding and extreme fastness to light are needed.

Oil stains dry and penetrate slowly so that brush marks can be readily wiped away. The preliminary sponging and sanding treatments of the wood required when water stains are used are unnecessary with oil stains as the latter show little tendency to raise the wood grain. Oil stains are used on interior woodwork, concrete, and wood floors, for the inside surfaces of drawers, and for refinishing furniture. (See Tables V, VIII, X for formulas.)

### Spirit Stains

Spirit stains are  $\frac{1}{2}$  to 12 per cent solutions of dyes in alcoholic solutions of shellac or other spirit-soluble resins, although occasionally they are used without binders present. They tend to dry quickly so that considerable skill is required to apply them evenly to large areas. They are used to finish the insides of cabinets and for refinishing pieces when it is necessary to penetrate through old finishes. They are much used for toys, but today there is a growing tendency to use certified dyes in articles for children (29). (See Tables V, IX, X for some formulas.)

### Non-Grain-Raising Stains

These are the most recently developed wood stains, and into their formulation may go selected mixtures of the several hundred modern solvents. Unfortunately, at present their formulation is thoroughly



TABLE VIII  
PENETRATING OIL STAINS: COLOR FORMULAS

(Note: The proportions shown represent ounces per one gallon of thinned stain.)

	Colour Index Number	Red Mahogany	Red-wood	Light Rose-wood	Dark Rose-wood	Dark Mahogany	Light Brown Mahogany	Cherry
Oil Red N-1700	Note A	1.25	0.5	0.125	1.125	0.25	0.125	0.125
Oil Orange 7078	Note B	1.25	0.5	0.200	0.500	1.25	1.625	2.875
Oil Black 8603	Note C			0.175	1.875	1.00	0.750	
Ratio: Grams per 100 cc.	Note F	2.0	0.6	0.4	2.0	2.0	2.0	2.0
Maerz & Paul Plate	Note G	3L9	3K9	5J9	5K9	7J10	6K11	2L12

	Colour Index Number	Cedar	Walnut	Walnut Shell	Maple	Light Golden Oak	Oak	Weathered Oak	Dark Green
Oil Red N-1700	Note A	0.125			0.025				
Oil Orange 7078	Note B	1.750	1.625	0.175	0.225	0.0375	1.625		
Oil Black 8603	Note C	0.625	0.875	0.225	0.050		0.750	0.90	
Oil Yellow 7463	19			0.100	0.200	0.2125	0.125	0.05	
Oil Blue B-5199	Note D							0.05	
Oil Blue NA	Note E								0.7
Auramine O Conc.	655								1.8
Ratio: Grams per 100 cc.	Note F	2.0	2.0	0.4	0.4	0.2	2.0	0.8	2.0
Maerz & Paul Plate	Note G	6G10	6C10	12E6	10K9	10L7	14A11	39A1	23J12

Notes: Nearest similar Colour Index dye

A. Sudan III C.I. 248

B. Sudan I C.I. 24

C. Nigrosine stearate C.I. 864

D. Induline stearate C.I. 880

E. This is an anthraquinone base dye.

F. These are the grams of the total dye mixture to use for 100 milliliters of thinned stain. Multiply these by 1.25 to get total ounces per gallon.

G. These are the color plates selected by the author from Maerz and Paul's *Dictionary of Color* as representing closely the currently conventional wood colors.

H. These formulations were derived from work on birch, a wood that has a light brown self-shade. If applied to wood with a darker or lighter self-shade or to wood that is more porous, or to materials other than wood, the formulas should be altered as may seem advisable.

J. These formulas may be used as the basis of one-coat *varnish stains*, also. Some adjustments may be necessary if the self-shade of the varnish is a strong color. The thickness of the varnish film applied is also an important factor.

TABLE VIII—*Continued*  
 LACQUER STAINS: COLOR FORMULAS (*see Note E*)

*Wood Colors with Oil-Soluble Dyes*

	Colour Index Number	Red Mahogany	Dark Brown Mahogany	Cedar	Walnut Shell	Oak	Golden Oak	Maple	Weathered Oak
Oil Red O-5078	Note A	50	8	5			5	8	
Oil Orange 7078	Note B	50	50	65	50	65	15	40	
Oil Black 8603	Note C		42	30	50	30		15	75
Oil Yellow 7463	19					5	80	37	4
Oil Blue B-5199	Note D								21
Approx. Ounces per Gallon	Note F	2½	0.75	0.75	0.20	0.25	0.375	0.3	0.375

Notes: Nearest similar Colour Index dye

A. Sudan III C.I. 248

B. Sudan I C.I. 24

C. Nigrosine stearate C.I. 864

D. Induline stearate C.I. 860

E. These proportions are in parts per 100 of the dry dye mixtures. The individual dye ingredients may be dry-blended together to form proprietary dyestuff mixtures.

F. The amount of the total dye mixture to use will vary greatly with the percentage of film-forming materials in the lacquer, and the actual thickness of film applied, so that these figures are for trial guidance only.

blanketed by patents (41). Their name, non-grain-raising stains, is doubtless derived from the fact that they show a minimum tendency to raise the wood grain. Because of this feature, their use eliminates much of the back-breaking labor and the production time formerly required in sanding operations.

Essentially, these stains are solutions of the acid dyes and/or selected spirit-soluble dyes in non-aqueous vehicles. The stains are comprised of ½ to 6 per cent of dyestuff, 5 to 10 per cent of dye solvent, 20 to 50 per cent of alcohols, and the remainder of medium-boiling hydrocarbons or other liquids non-miscible with water. The dye solvent is usually a mixture of medium-to-high-boiling or practically non-volatile liquids, and so are the last fraction to evaporate, thereby maintaining the dye in solution long enough to stain the wood. If too great a proportion of these liquids is used, they may first penetrate into the wood, then spew or more often slowly sweat or exude to the surface and loosen any top-coating films. The diethyl ether of ethylene glycol and methyl lactate are two of the better ingredients used as dye solvents. Others are ethylene glycol, diethyl-

TABLE IX  
SPIRIT STAINS

	Red	Orange	Yellow	Green	Blue	Brown	Gold
Fast Spirit Red B	1 oz.						
Fast Spirit Org. R Conc.		$\frac{3}{4}$ oz.					0.05 oz.
Fast Spirit Yellow 2R Conc.		$\frac{1}{4}$ oz.	1 oz.				0.35 oz.
Fast Spirit Brown G						1 oz.	0.10 oz.
Fast Spirit Blue GI. *				1 $\frac{1}{2}$ oz.	2 oz.		
Fast Spirit Yellow 3GX *				3 $\frac{3}{4}$			
Alcohol	2 qt.	2 qt.	2 qt.	1 qt.	1 qt.	2 qt.	2 qt.
Ethyl Ether of Ethylene Glycol				1 qt.	1 qt.		
Refined Shellac Sol. (5 lb. per cut)†	2 qt.	2 qt.	2 qt.	2 qt.	2 qt.	2 qt.	2 qt.

\* Contain some inorganic salts which can be readily settled out.

† Can be replaced with lacquers that tolerate large additions of alcohol, or solutions of other spirit soluble resins.

*Water Fast Spirit Stains*

Dybryte Red X ‡	3 oz.
Alcohol	2 qt.
Water	2 qt.

*High Gloss Spirit Stains*

Rhodamine B Base §	1 oz.
Alcohol	3 qt.
Shellac Solution (5 lb. per cut)	1 qt.

‡ Use the same formula for:

Dybryte Pink O-2023, Dybryte Orange X, Dybryte Yellow X, Dybryte Green X, Dybryte Sky Blue X, Dybryte Blue X, Dybryte Violet N-4339

§ Use the same formula for:

Chrysoidine Base, Auramine Base, Victoria Green Base, Victoria Blue Base, Methyl Violet Base, Nigrosine SSB (2 oz.), and Nigrosine SSJ (2 oz.)

ene glycol and the monomethyl, monoethyl, and isopropyl ethers of ethylene glycol and propylene glycol. Acetone and other ketones also have been used for this purpose.

These stains yield bright, transparent, and light-resistant effects. They can be formulated to be non-toxic and to have very little odor. Their use is growing for all types of high-quality wood-staining applications. (See Table XI.)

### THE BASIS OF STAIN SELECTION

The selection of the type of stain to use for any specific wood-staining application is based chiefly on their following major features:

	Principal Vehicle	Effect on Wood Grain	Toxicity	Fastness to Light	Bleeding	
					Top Coats	Water
Water-soluble	Water	Raises	None	Good	None	Bleed
Oil-soluble stains	Hydro-carbons	Non-raising	Toxic	Moderate	May bleed	None
Spirit-soluble	Alcohols	Raises slightly	Usually slight	Moderate	Bleed	Vary widely
Non-grain-raising	Mixed Non-aqueous	Non-raising	Varies widely	Good	Bleed	May bleed

The water-soluble stains are lowest in cost, but this advantage is largely balanced by the sanding operations concomitant to their use. They have good fastness to light and a minimum tendency to bleed into varnish and lacquer top coatings. The color intensity of these stains can be controlled easily by simply wiping off the excess color with a wet cloth.

The non-grain-raising stains are high in cost, but this is often balanced by the saving of labor for sanding operations. They may contain the same dyes as any one or all of the other three groups, as they can be formulated to dissolve water-, spirit-, and oil-soluble dyes to a large degree. They combine the features of all the other stains.

The oil-soluble stains are moderate in cost, considering that they have non-aqueous vehicles. They are an older, special group of non-grain-raising stains. Their use avoids some sanding operations, and they also can be readily incorporated in varnishes or lacquers to fill, prime, and stain in one operation. Their fastness to light is moderate to good. Their pronounced anti-oxidant effects delay varnish drying greatly.

The spirit-soluble stains are the third highest cost group. They cut through old finishes well, dry quickly, and can be formulated to be non-bleeding in water. They are used on shipping containers, baskets, inside rough-finished surfaces, drawers, and toys. Their principal applications, however, are in other fields, notably paper and leather staining, and high-speed press inks.

While most stainers use one or more of these four types of stains, the ingredient colors and vehicles available are so numerous and varied in properties that there is a wide scope for the technical knowledge and ingenuity of the formulator and colorist. Moreover, the almost infinite variety of modern materials on which stains are used insures an unending series of stain-development problems.

TABLE X—Continued

Lacquer and Varnish Stain Dyes	Red	Scarlet	Orange	Yellow	Green	Blue	Violet	Red	Scarlet	Orange	Yellow	Green	Blue	Violet
D&C Red No. 18	oz. $\frac{1}{2}$	oz. $\frac{1}{10}$	oz.	oz.	oz.	oz.	oz.	oz. $2\frac{1}{2}$	oz.	oz.	oz.	oz.	oz.	oz.
FD&C Red No. 32		$\frac{2}{8}$							$2\frac{1}{2}$					
FD&C Orange No. 2			$\frac{1}{2}$							$2\frac{1}{2}$				
FD&C Yellow No. 5				$\frac{1}{2}$	$\frac{1}{8}$						$2\frac{1}{2}$	1		
Ext. D&C Blue No. 5					$\frac{3}{10}$	$\frac{1}{2}$						$1\frac{1}{2}$	$2\frac{1}{2}$	
Ext. D&C Violet							$\frac{1}{2}$							$2\frac{1}{2}$
Lacquer Thinner	2 qt.	2 qt.	2 qt.	2 qt.	2 qt.	2 qt.	2 qt.							
Lacquer Base	2 qt.	2 qt.	2 qt.	2 qt.	2 qt.	2 qt.	2 qt.							
Varnish Thinner								1 qt.	1 qt.	1 qt.	1 qt.	1 qt.	1 qt.	1 qt.
Varnish Base								3 qt.	3 qt.	3 qt.	3 qt.	3 qt.	3 qt.	3 qt.

Note: Dissolve the dyes in the thinners, warming if necessary, then stir into the base lacquer or varnish.

TABLE XI  
NON-GRAIN RAISING WOOD STAINS

Fast Spirit Stains	Red Mahogany	Walnut	Satin-wood *
Fast Spirit Red B	33		
Fast Spirit Orange R Conc.	55	23	10
Fast Spirit Yellow 2R Conc.		55	85
Fast Spirit Blue GL	12	22	5
Ounces per gallon	8 oz.	8 oz.	1¼ oz.

\* This formula is often diluted and used to tint hardwood interior trim.

Acid Color Stains †	C.I. Number	Red Mahogany	Brown Mahogany	Walnut	Oak	Dark Green
Acid Brill. Red B	32	60	15	5		
Orange II	151	40	55	65	55	15
Acid Blue Black	246		30	30	8	35
Metanil Yellow	138				37	25
Naphthol Yellow S	10					25
Ounces per gallons		2½	2½	2½	2½	2½

† These dyes are best used with ethylene glycol, its monoethyl ether, or the similar ether of diethylene glycol as the principal solvents.

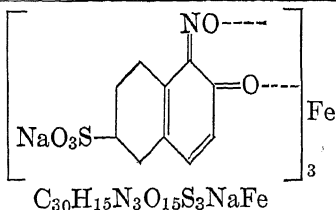
## STAINING REMAINS AN ART

Stainers today probably can obtain no effects greatly superior to those of the older craftsmen, but they do have the stains that enable them to get results more easily, more quickly, more safely, and at minimum labor costs. There still is, however, no substitute for the artistry required in their use. Stains must be applied skillfully and

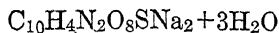
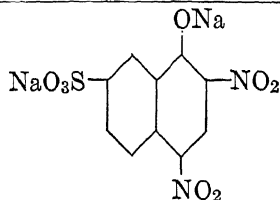
## XII

## TYPICAL SYNTHETIC DYES

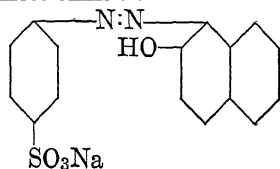
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 Application Group: Acid Dye  
 C.I.-5 Naphthol Green B



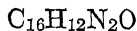
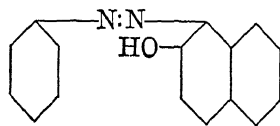
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 Application Group: Acid Dye  
 C.I.-10 Naphthol Yellow S



Chemical Group: Azo  
 Application Group: Acid Dye  
 C.I.-151 Acid Orange II



Chemical Group: Azo  
 Application Group: Oil-Soluble  
 Dye  
 C.I.-24 Sudan I (Oil Orange)



Chemical Group: Azostilbene  
 Application Group: Direct Dye  
 C.I.-621 Direct (Stilbene) Orange

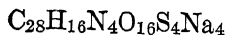
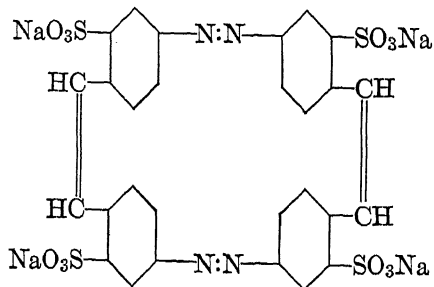
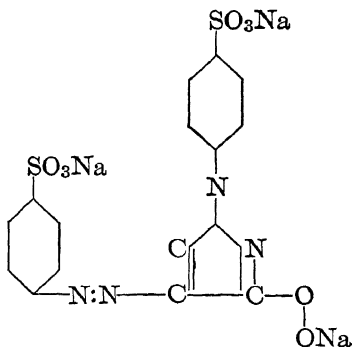
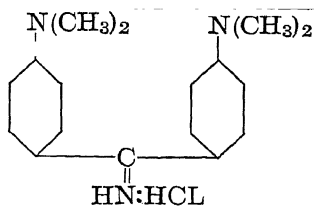


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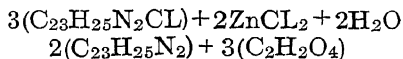
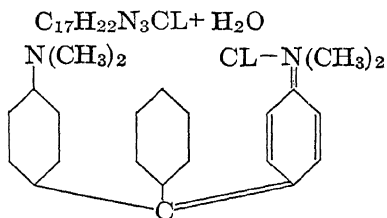
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 Application Group: Acid Dye  
 C.I.-640 Tartrazine



Chemical Group: Ketonimine  
 Application Group: Basic Dye  
 C.I.-655 Auramine



Chemical Group: Triphenyl-  
methane  
 Application Group: Basic Dye  
 C.I.-657 Malachite Green  
 Double Zinc Chloride  
 Oxalate



Chemical Group: Triphenyl-  
methane  
 Application Group: Organic Pig-  
ment  
 C.I.-704 Alkali Blue  
 (Monosulfonic Acid)

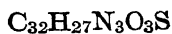
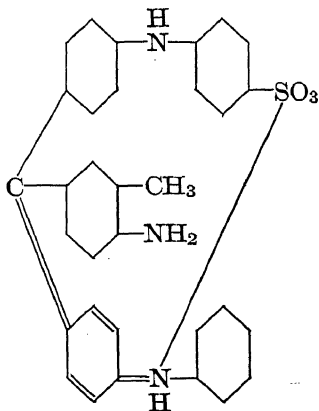
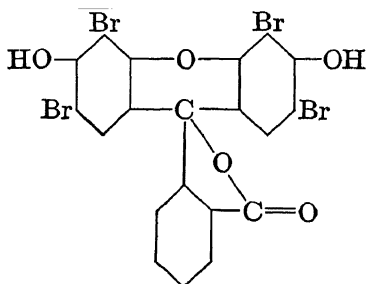


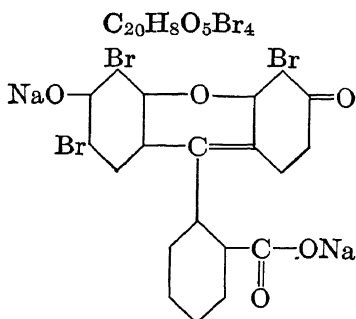


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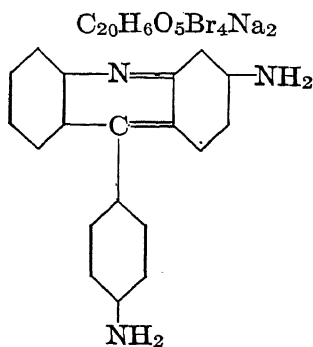
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 Application Group: Organic Pigment  
 C.I.-768 Tetrabromofluorescein  
 (Bromo Acid)



Chemical Group: Xanthene  
 Application Group: Acid Dye  
 C.I.-768 Eosine (Sodium Salt  
 Tetrabromofluorescein)



Chemical Group: Acridine  
 Application Group: Basic Dye  
 C.I.-793 Phosphine Base



Chemical Group: Quinoline  
 Application Group: Spirit-Soluble Dye  
 C.I.-800 Quinoline Yellow SS

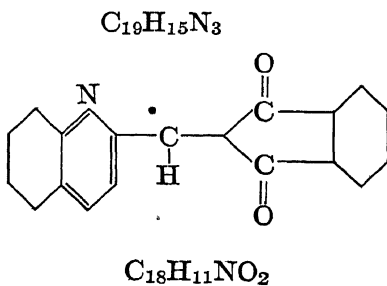
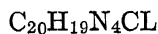
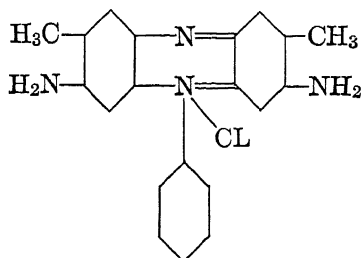
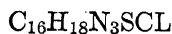
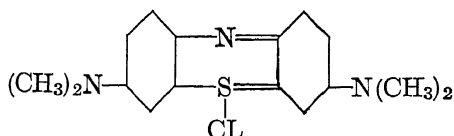


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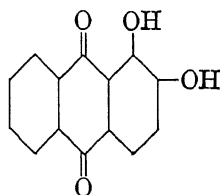
Chemical Group: Azine  
 Application Group: Basic Dye  
 C.I.-841 Safranine



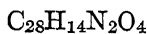
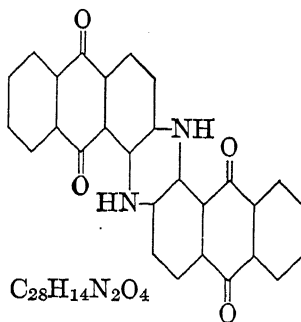
Chemical Group: Thiazine  
 Application Group: Basic Dye  
 C.I.-922 Methylene Blue



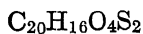
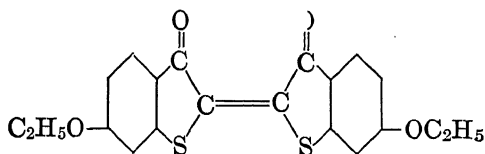
Chemical Group: Anthraquinone  
 (Hydroxy Ketone)  
 Application Group: Acid Mor-  
 dant Dye  
 C.I.-1027 Alizarine



Chemical Group: Anthraquinone-  
 Azine  
 Application Group: Vat Dye  
 C.I.-1106 Indanthrene Blue RS  
 (Indanthrone)



Chemical Group: Thioindigoid  
 Application Group: Vat Dye  
 C.I.-1217 Helindone (Hydron)  
 Orange R



with adequate compensation for differences in the surface self-shade, variations of structure, absorption, and the many other properties of surfaces, and in accordance with the laws of color harmony and designing. Technological advances have made the formulation of stains an example of applied science; their use still remains an art.

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